S/N 10/568,739

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                  Zentralblatt
 NEWS  3  OCT 19  BEILSTEIN updated with new compounds
 NEWS  4  NOV 15  Derwent Indian patent publication number format enhanced
 NEWS  5  NOV 19  WPIX enhanced with XML display format
 NEWS  6  NOV 30  ICSD reloaded with enhancements
 NEWS  7  DEC 04  LINPADOCDB now available on STN
 NEWS  8  DEC 14  BEILSTEIN pricing structure to change
 NEWS  9  DEC 17  USPATOLD added to additional database clusters
 NEWS 10  DEC 17  IMSDRUGCONF removed from database clusters and STN
 NEWS 11  DEC 17  DGENE now includes more than 10 million sequences
 NEWS 12  DEC 17  TOXCENTER enhanced with 2008 MeSH vocabulary in
                  MEDLINE segment
 NEWS 13  DEC 17  MEDLINE and LMEDLINE updated with 2008 MeSH vocabulary
 NEWS 14  DEC 17  CA/CAplus enhanced with new custom IPC display formats
 NEWS 15  DEC 17  STN Viewer enhanced with full-text patent content
                  from USPATOLD
 NEWS 16  JAN 02  STN pricing information for 2008 now available
 NEWS 17  JAN 16  CAS patent coverage enhanced to include exemplified
                  prophetic substances
 NEWS 18  JAN 28  USPATFULL, USPAT2, and USPATOLD enhanced with new
                  custom IPC display formats
 NEWS 19  JAN 28  MARPAT searching enhanced
 NEWS 20  JAN 28  USGENE now provides USPTO sequence data within 3 days
                  of publication
 NEWS 21  JAN 28  TOXCENTER enhanced with reloaded MEDLINE segment
 NEWS 22  JAN 28  MEDLINE and LMEDLINE reloaded with enhancements
 NEWS 23  FEB 08  STN Express, Version 8.3, now available
 NEWS 24  FEB 20  PCI now available as a replacement to DPCI
 NEWS 25  FEB 25  IFIREF reloaded with enhancements
 NEWS 26  FEB 25  IMSPRODUCT reloaded with enhancements
 NEWS 27  FEB 29  WPINDEX/WPIDS/WPIX enhanced with ECLA and current
                  U.S. National Patent Classification


 NEWS EXPRESS FEBRUARY 08 CURRENT WINDOWS VERSION IS V8.3,
              AND CURRENT DISCOVER FILE IS DATED 20 FEBRUARY 2008

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=> set plurals on pemr
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=> set plurals on perm
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=> set abbr on perm
SET COMMAND COMPLETED

=> file uspatall caplus japio
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                                                       ENTRY   SESSION
FULL ESTIMATED COST                                     0.42      0.42

FILE 'USPATFULL' ENTERED AT 15:47:51 ON 21 MAR 2008
CA INDEXING COPYRIGHT (C) 2008 AMERICAN CHEMICAL SOCIETY (ACS)

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FILE 'JAPIO' ENTERED AT 15:47:51 ON 21 MAR 2008
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=> s ((ethylene or ethene)(4a)(polymer or copolymer) or (polyethylene or
polyethene))(s)(trimodal? or tri(1w)modal? or tetramodal? or tetra(1w)modal?)
L1           88 ((ETHYLENE OR ETHENE)(4A)(POLYMER OR COPOLYMER) OR (POLYETHYLENE
                 OR POLYETHENE))(S)(TRIMODAL? OR TRI(1W) MODAL? OR TETRAMODAL?
                OR TETRA(1W) MODAL?)

=> s (ethylene or ethene)(3a)(copolymer or interpolymer)
L2       289976 (ETHYLENE OR ETHENE)(3A)(COPOLYMER OR INTERPOLYMER)

=> s l1 and l2
L3           70 L1 AND L2

=> s l3 and melt index
L4           37 L3 AND MELT INDEX
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S/N 10/568,739

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=> s l4 and (melt or mif)(4a)ratio#
L5          21 L4 AND (MELT OR MIF)(4A) RATIO#

=> d l5 1-21 ibib abs

L5   ANSWER 1 OF 21  USPATFULL on STN
ACCESSION NUMBER:        2007:322750  USPATFULL
TITLE:                   Process for the (Co) Polymerization of Ethylene
INVENTOR(S):             Baita, Pietro, Occhiobello, ITALY
                         Covezzi, Massimo, Ferrara, ITALY
                         Mei, Gabriele, Ferrara, ITALY
                         Morini, Giampiero, Padova, ITALY
                         Pater, Joachim T.M., Ferrara, ITALY
PATENT ASSIGNEE(S):      Basell Polyolefine GmbH, Wesseling, GERMANY, FEDERAL
                         REPUBLIC OF, DE 50389 (non-U.S. corporation)

                              NUMBER        KIND    DATE
                         ---------------- ------ --------
PATENT INFORMATION:      US 2007282083      A1   20071206
APPLICATION INFO.:       US 2004-581983     A1   20041124  (10)
                         WO 2004-EP13372         20041124
                                                 20060607  PCT 371 date

                                NUMBER        DATE
                         ------------------ --------
PRIORITY INFORMATION:    EP 2003-104854     20031219
                         US 2003-532128P    20031222 (60)
DOCUMENT TYPE:           Utility
FILE SEGMENT:            APPLICATION
LEGAL REPRESENTATIVE:    BASELL USA INC., INTELLECTUAL PROPERTY, 912 APPLETON
                         ROAD, ELKTON, MD, 21921, US
NUMBER OF CLAIMS:        14
EXEMPLARY CLAIM:         1
LINE COUNT:              818
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB       A process for preparing a broad molecular weight polyethylene carried
       out in the presence of a catalyst system comprising (i) a solid catalyst
       component comprising Mg, Ti, halogen, and optionally an internal
       electron donor compound, and (ii) an Al-alkyl cocatalyst said process
       comprising at least two step of polymerization (a) and (b), in which: in
       a first step (a) ethylene is polymerized in the presence of a molecular
       weight regulator in order to produce a ethylene (co)polymer, and in a
       further step (b), which is carried out in the presence of an external
       electron donor compound added to this polymerization step as a fresh
       reactant, ethylene is copolymerized with an alpha olefin of formula
       CH2.dbd.CHR, in which R is a C1-C20 hydrocarbon group, to produce an
       ethylene copolymer having a molecular weight higher
       than that of the copolymer produced in step (b).

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5   ANSWER 2 OF 21  USPATFULL on STN
ACCESSION NUMBER:        2007:128803  USPATFULL
TITLE:                   Multimodal polyethylene material
INVENTOR(S):             Schramm, Detlef, Hombrechtikon, SWITZERLAND
                         Quack, Wolfgang, Mettmann, GERMANY, FEDERAL REPUBLIC OF
                         Damen, Julien, Mettmenstetten, SWITZERLAND
                         Cham, Pak-Meng, Lake Jackson, TX, UNITED STATES
PATENT ASSIGNEE(S):      Dow Global Technologies Inc., Midland, MI, UNITED
                         STATES (non-U.S. corporation)
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	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2007112160	A1	20070517	
APPLICATION INFO.:	US 2006-634503	A1	20061206	(11)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2004-484906, filed on 10 Aug 2004, PENDING A 371 of International Ser. No. WO 2002-US27503, filed on 28 Aug 2002

	NUMBER	DATE
PRIORITY INFORMATION:	US 2001-316401P	20010831 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: THE DOW CHEMICAL COMPANY, INTELLECTUAL PROPERTY SECTION,, P. O. BOX 1967, MIDLAND, MI, 48641-1967, US
NUMBER OF CLAIMS: 15
EXEMPLARY CLAIM: 1-3
LINE COUNT: 697
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention relates to a polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it has a density in the range of from about 0.925 g/ccm to about 0.950 g/ccm, a melt index (I.sub.2)
In the range of from about 0.05 g/10 min to about 5 g/10 min, and in that it comprises at least one high molecular weight (HMW) ethylene interpolymer and at least a low molecular weight (LMW) ethylene polymer, and a composition comprising such resin. Also provided is a shaped article comprising said resin or composition, in particular a pipe.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 3 OF 21 USPATFULL on STN
ACCESSION NUMBER: 2007:107648 USPATFULL
TITLE: Process and apparatus for the polymerization of ethylene
INVENTOR(S): Meier, Gerben, Frankfurt, GERMANY, FEDERAL REPUBLIC OF
Covezzi, Massimo, Ferrara, ITALY
Baita, Pietro, Rovigo, ITALY
Mei, Gabriele, Ferrara, ITALY
PATENT ASSIGNEE(S): BASELL POLIOLEFINE ITALIA S.R.L., Milan, ITALY, 20124 (non-U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2007093621	A1	20070426	
APPLICATION INFO.:	US 2004-568739	A1	20040719	(10)
	WO 2004-EP8063		20040719	
			20060217	PCT 371 date

	NUMBER	DATE
PRIORITY INFORMATION:	EP 2003-77645	20030820
	US 2003-497900P	20030825 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: BASELL USA INC., INTELLECTUAL PROPERTY, 912 APPLETON ROAD, ELKTON, MD, 21921, US
NUMBER OF CLAIMS: 25

EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 2 Drawing Page(s)
LINE COUNT: 1126
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Process for preparing a broad molecular weight polyethylene by polymerizing ethylene in the presence of a polymerization catalyst, the process comprising the following steps, in any mutual order: a) polymerizing ethylene, optionally together with one or more α-olefinic comonomers having from 3 to 12 carbon atoms, in a gas-phase reactor in the presence of hydrogen, b) copolymerizing ethylene with one or more α-olefinic comonomers having from 3 to 12 carbon atoms in another gas-phase reactor in the presence of an amount of hydrogen less than step a), where in at least one of said gas-phase reactors the growing polymer particles flow upward through a first polymerization zone under fast fluidization or transport conditions, leave said first polymerization zone and enter a second polymerization zone through which they flow downward under the action of gravity.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 4 OF 21 USPATFULL on STN
ACCESSION NUMBER: 2007:56765 USPATFULL
TITLE: Catalyst compositions comprising support materials having an improved particle-size distribution

INVENTOR(S): Kuo, Chi-I, Humble, TX, UNITED STATES
Kwalk, Tae Hoon, Belle Mead, NJ, UNITED STATES
Li, Dongming, Houston, TX, UNITED STATES
Shannon, Porter Clarke, Seabrook, TX, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2007049711	A1	20070301	
APPLICATION INFO.:	US 2005-218213	A1	20050901	(11)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: Univation Technologies, LLC, Suite 1950, 5555 San Felipe, Houston, TX, 77056, US
NUMBER OF CLAIMS: 24
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 1 Drawing Page(s)
LINE COUNT: 2234
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyst composition that includes a support material having an improved particle-size distribution is provided. Processes for producing polyolefin composition also are provided. Polymers and films also are provided. An example of a catalyst composition is a supported multi-transition-metal catalyst composition that includes: (a) at least two catalyst components selected from the group consisting of: a nonmetallocene catalyst component and a metallocene catalyst component; (b) a support material that has a D.sub.50 of less than about 30 microns and a particle size distribution having a D.sub.90/D.sub.10 ratio of less than about 6; and (c) an activator.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 5 OF 21 USPATFULL on STN
ACCESSION NUMBER: 2007:24522 USPATFULL
TITLE: Bimodal polyethylene composition and articles made therefrom

```
INVENTOR(S):            Van Dun, Jozef J., Zandhoven, BELGIUM
                        van den Berghe, Peter F.M., Graauw, NETHERLANDS
                        Schouterden, Patrick J., Wachtebeke, BELGIUM
                        Nicasy, Ruddy, Westerlo, BELGIUM
                        Vanvoorden, Johan, Diepenbeek, BELGIUM
                        Gemoets, Frederik E.L., Wommelgem, BELGIUM
                        Sehanobish, Kalyan, Lake Jackson, TX, UNITED STATES
                        Jivraj, Noorallah, Lake Jackson, TX, UNITED STATES
                        Dixit, Ravi S., Lake Jackson, TX, UNITED STATES
PATENT ASSIGNEE(S):     Dow Global Technologies Inc., Midland, MI, UNITED
                        STATES (U.S. corporation)

                             NUMBER       KIND    DATE
                        ---------------- ------ --------
PATENT INFORMATION:     US 2007021567      A1   20070125
                        US 7345113         B2   20080318
APPLICATION INFO.:      US 2006-480091     A1   20060630  (11)
RELATED APPLN. INFO.:   Continuation of Ser. No. US 2004-817030, filed on 2 Apr
                        2004, GRANTED, Pat. No. US 7129296 Continuation of Ser.
                        No. US 2002-222273, filed on 16 Aug 2002, GRANTED, Pat.
                        No. US 6787608

                               NUMBER        DATE
                        ------------------ --------
PRIORITY INFORMATION:   US 2001-313357P    20010817 (60)
                        US 2001-313176P    20010817 (60)
DOCUMENT TYPE:          Utility
FILE SEGMENT:           APPLICATION
LEGAL REPRESENTATIVE:   THE DOW CHEMICAL COMPANY, INTELLECTUAL PROPERTY
                        SECTION,, P. O. BOX 1967, MIDLAND, MI, 48641-1967, US
NUMBER OF CLAIMS:       17
EXEMPLARY CLAIM:        1-54
NUMBER OF DRAWINGS:     6 Drawing Page(s)
LINE COUNT:             2145
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
```

AB The invention relates to a polyethylene composition with a bimodal molecular weight distribution, methods for making the same, and articles made therefrom, such as high topload blow moldings and transmission and distribution pipes. The composition comprises a low-molecular-weight (LMW) ethylene homopolymer component and a homogeneous, high-molecular-weight (HMW) ethylene interpolymer component, wherein the LMW component is characterized as having a molecular weight distribution, MWD.sup.L, of less than about 8. In some embodiments, the HMW component is characterized by a reverse comonomer distribution.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

```
L5   ANSWER 6 OF 21  USPATFULL on STN
ACCESSION NUMBER:       2006:47599  USPATFULL
TITLE:                  Polymer compositions and method of making pipes
INVENTOR(S):            Zhou, Zhiqiang Jimmy, Somerset, NJ, UNITED STATES
                        Michie, William J. JR., Missouri City, TX, UNITED
                        STATES
PATENT ASSIGNEE(S):     Union Carbide Chemicals & Plastics Technology
                        Corporation, Danbury, CT, UNITED STATES, 06817-0001
                        (U.S. corporation)

                             NUMBER       KIND    DATE
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PATENT INFORMATION: US 2006041073 A1 20060223
APPLICATION INFO.: US 2005-202756 A1 20050812 (11)
RELATED APPLN. INFO.: Continuation of Ser. No. US 2003-454049, filed on 4 Jun 2003, ABANDONED

	NUMBER	DATE
PRIORITY INFORMATION:	US 2002-386291P	20020604 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: BAKER & MCKENZIE LLP, 711 LOUISIANA, SUITE 3400, HOUSTON, TX, 77002-2716, US
NUMBER OF CLAIMS: 25
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 3 Drawing Page(s)
LINE COUNT: 1441
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A polymer composition comprises a low-molecular-weight (LMW) ethylene polymer component and a high-molecular-weight (HMW) ethylene polymer component. Preferably, the LMW polyethylene component and the HMW polyethylene component co-crystallize in the composition such that it exhibits a single or substantially single peak in a lamella thickness distribution ("LTD") curve. The ethylene polymer for the LMW and the HMW polyethylene components can be either homopolyethylene or ethylene copolymer. Preferably, both components are an ethylene copolymer of the same or different composition (i.e., with the same or different comonomers). A method of making a pipe that includes selecting a polymer composition having a substantially single peak in the LTD curve is described.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 7 OF 21 USPATFULL on STN
ACCESSION NUMBER: 2006:41389 USPATFULL
TITLE: High strength bimodal polyethylene compositions
INVENTOR(S): Kwalk, Tae Hoon, Belle Mead, NJ, UNITED STATES

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 2006036041	A1	20060216
	US 7193017	B2	20070320
APPLICATION INFO.:	US 2004-918190	A1	20040813 (10)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: Attn: Kevin Faulkner, Univation Technologies, LLC, Suite 1950, 5555 San Felipe, Houston, TX, 77056, US
NUMBER OF CLAIMS: 26
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 1 Drawing Page(s)
LINE COUNT: 1074
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Disclosed are various compositions, including but not limited to a high strength bimodal polyethylene composition having a density of 0.940 g/cc or more, the composition comprising a high molecular weight polyethylene component having a higher weight average molecular weight (Hw.sub.HMW) and a low molecular weight polyethylene component having a lower weight average molecular weight (Hw.sub.LMW), wherein: the ratio of the higher weight average molecular weight to the lower weight average molecular weight (Mw.sub.HMW:Mw.sub.LMW) is 30 or more; and the composition qualifies as a PE 100 material such that in accordance with ISO 1167 a

pipe formed from the composition that is subjected to internal pipe resistance has an extrapolated stress of 10 MPa or more when the internal pipe resistance curve is extrapolated to 50 or 100 years in accordance with ISO 9080:2003(E).

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 8 OF 21 USPATFULL on STN
ACCESSION NUMBER: 2005:325066 USPATFULL
TITLE: Copolymers of ethylene with alpha-olefins
INVENTOR(S): Mihan, Shahram, Bad Soden, GERMANY, FEDERAL REPUBLIC OF
Lilge, Dieter, Limburgerhof, GERMANY, FEDERAL REPUBLIC OF

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2005282979	A1	20051222	
APPLICATION INFO.:	US 2003-538540	A1	20031218	(10)
	WO 2003-EP14437		20031218	
			20050611	PCT 371 date

	NUMBER	DATE
PRIORITY INFORMATION:	DE 2002-10261252	20021220
	US 2003-60451836	20030304

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: BASELL USA INC., INTELLECTUAL PROPERTY, 912 APPLETON ROAD, ELKTON, MD, 21921, US
NUMBER OF CLAIMS: 15
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 2 Drawing Page(s)
LINE COUNT: 2437
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Copolymers of ethylene with α-olefins which have a molar mass distribution M.sub.w/M.sub.a of from 1 to 8, a density of from 0.85 to 0.94 g/cm.sup.3, a molar mass M.sub.a of from 10,000 g/mol to 4 000 000 g/mol and a CDBI of less than 50% and in which the side chain branching of the maxima of the individual peaks of the short chain branching distribution is in each case greater than 5 CH.sub.3/1 000 carbon atoms, a process for preparing them, a catalyst suitable for preparing them and fibers, moldings, films or polymer mixtures in which these copolymers are present

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 9 OF 21 USPATFULL on STN
ACCESSION NUMBER: 2004:335871 USPATFULL
TITLE: Multimodal polyolefin pipe
INVENTOR(S): Schramm, Detlef, Hombrechtihen, SWITZERLAND
Quack, Wolfgang, Mettmann, GERMANY, FEDERAL REPUBLIC OF
Damen, Julien, Mettmenstetten, SWITZERLAND
Cham, Pak-Meng, Lake Jackson, TX, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2004266966	A1	20041230	
	US 7250473	B2	20070731	
APPLICATION INFO.:	US 2004-484906	A1	20040810	(10)

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                        WO 2002-US27503        20020828

                               NUMBER        DATE
                        ------------------ --------
PRIORITY INFORMATION:   US 2001-60316401   20010831
DOCUMENT TYPE:          Utility
FILE SEGMENT:           APPLICATION
LEGAL REPRESENTATIVE:   THE DOW CHEMICAL COMPANY, INTELLECTUAL PROPERTY
                        SECTION, P. O. BOX 1967, MIDLAND, MI, 48641-1967
NUMBER OF CLAIMS:       10
EXEMPLARY CLAIM:        1
LINE COUNT:             697
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
```

AB The present invention relates to a polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it has a density in the range of from about 0.925 g/ccm to about 0.950 g/ccm, a melt index (I.sub.2)
in the range of from about 0.05 g/10 min to about 5 g/10 min, and in that it comprises at least one high molecular weight (HMW)
ethylene interpolymer and at least a low molecular
weight (LMW) ethylene polymer, and a composition comprising such resin. Also provided is a shaped article comprising said resin or composition, in particular a pipe.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

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L5   ANSWER 10 OF 21  USPATFULL on STN
ACCESSION NUMBER:       2004:255381  USPATFULL
TITLE:                  Bimodal polyethylene pipe composition and article made
                        therefrom
INVENTOR(S):            Van Dun, Jozef J., Missouri City, TX, UNITED STATES
                        Schouterden, Patrick J., Wachtebeke, BELGIUM
                        Sehanobish, Kalyan, Lake Jackson, TX, UNITED STATES
                        van den Berghen, Peter F. M., Graauw, NETHERLANDS
                        Jivraj, Noorallah, Lake Jackson, TX, UNITED STATES
                        Nicasy, Ruddy, Westerlo, BELGIUM
                        Vanvoorden, Johan, Diepenbeek, BELGIUM
                        Dixit, Ravi S., Lake Jackson, TX, UNITED STATES
                        Gemoets, Frederik E., Wommelgem, BELGIUM

                             NUMBER       KIND    DATE
                        ---------------- ------ --------
PATENT INFORMATION:     US 2004198911      A1   20041007
                        US 7129296         B2   20061031
APPLICATION INFO.:      US 2004-817030     A1   20040402  (10)
RELATED APPLN. INFO.:   Continuation of Ser. No. US 2002-222273, filed on 16
                        Aug 2002, PENDING

                               NUMBER        DATE
                        ------------------ --------
PRIORITY INFORMATION:   US 2001-313176P    20010817 (60)
                        US 2001-313357P    20010817 (60)
DOCUMENT TYPE:          Utility
FILE SEGMENT:           APPLICATION
LEGAL REPRESENTATIVE:   JENKENS & GILCHRIST, 1401 MCKINNEY, SUITE 2600,
                        HOUSTON, TX, 77010
NUMBER OF CLAIMS:       29
EXEMPLARY CLAIM:        CLM-01-54
NUMBER OF DRAWINGS:     6 Drawing Page(s)
LINE COUNT:             2242
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S/N 10/568,739

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to a polyethylene composition with a bimodal molecular weight distribution and articles made therefrom. The composition comprises a low-molecular-weight (LMW) ethylene homopolymer component and a homogeneous, high-molecular-weight (HMW) ethylene interpolymer component, wherein the LMW component is characterized as having a molecular weight distribution, MWD.sup.L, of less than about 8. In some embodiments, the HMW component is characterized by a reverse comonomer distribution.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 11 OF 21 USPATFULL on STN

ACCESSION NUMBER:	2004:45175 USPATFULL
TITLE:	Polymer compositions and method of making pipes
INVENTOR(S):	Zhou, Zhiqiang Jimmy, Belle Mead, NJ, UNITED STATES Michie, William J., JR., Missouri City, TX, UNITED STATES
PATENT ASSIGNEE(S):	Union Carbide Chemicals & Plastics Technology Corporation, Danbury, CT (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2004034169	A1	20040219	
APPLICATION INFO.:	US 2003-454049	A1	20030604	(10)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2002-386291P	20020604 (60)

DOCUMENT TYPE:	Utility
FILE SEGMENT:	APPLICATION
LEGAL REPRESENTATIVE:	JENKENS & GILCHRIST, 1401 MCKINNEY, SUITE 2700, HOUSTON, TX, 77010
NUMBER OF CLAIMS:	25
EXEMPLARY CLAIM:	1
NUMBER OF DRAWINGS:	3 Drawing Page(s)
LINE COUNT:	1456

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A polymer composition comprises a low-molecular-weight (LMW) ethylene polymer component and a high-molecular-weight (HMW) ethylene polymer component. Preferably, the LMW polyethylene component and the HMW polyethylene component co-crystallize in the composition such that it exhibits a single or substantially single peak in a lamella thickness distribution ("LTD") curve. The ethylene polymer for the LMW and the HMW polyethylene components can be either homopolyethylene or ethylene copolymer. Preferably, both components are an ethylene copolymer of the same or different composition (i.e., with the same or different comonomers). A method of making a pipe that includes selecting a polymer composition having a substantially single peak in the LTD curve is described.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 12 OF 21 USPATFULL on STN

ACCESSION NUMBER:	2003:266066 USPATFULL
TITLE:	High density polyethylene melt blends for improved stress crack resistance in pipe
INVENTOR(S):	Harris, Michael G., Findlay, OH, UNITED STATES

NUMBER	KIND	DATE

PATENT INFORMATION:	US 2003187083	A1	20031002	
	US 6822051	B2	20041123	
APPLICATION INFO.:	US 2002-112200	A1	20020329	(10)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: BARBARA E. ARNDT, PH.D., JONES, DAY, REAVIS & POGUE, NORTH POINT, 901 LAKESIDE AVENUE, CLEVELAND, OH, 44114
NUMBER OF CLAIMS: 44
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 1 Drawing Page(s)
LINE COUNT: 740
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention provides a polyethylene composition comprising a melt blend of (i) a bimodal high molecular weight high density polyethylene resin having a NCTL stress crack resistance of about 200 hours or greater, and (ii) a high density polyethylene resin selected from the group consisting of a homopolymer high density polyethylene resin, a copolymer high density polyethylene resin, and mixtures thereof, wherein the composition has a minimum NCTL stress crack resistance of 24 hours. In another embodiment, a polyethylene composition comprises a melt blend of the bimodal high molecular weight high density polyethylene resin and a linear low density polyethylene resin. The bimodal high molecular weight high density polyethylene resin can be a commodity film grade resin, the homopolymer and copolymer resins can be milk bottle grade and detergent bottle grade, respectively, and the linear low density polyethylene resin can be a film grade. The compositions are especially useful for manufacture of profile and corrugated pipe and/or pipe fitting applications, and chemical waste applications including sanitary sewer or irrigation piping systems.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 13 OF 21 USPATFULL on STN
ACCESSION NUMBER: 2003:214537 USPATFULL
TITLE: Bimodal polyethylene composition and articles made therefrom
INVENTOR(S): Van Dun, Jozef J., Missouri City, TX, UNITED STATES
Schouterden, Patrick J., Wachtebeke, BELGIUM
Sehanobish, Kalyan, Lake Jackson, TX, UNITED STATES
van den Berghe, Peter F.M., Graauw, NETHERLANDS
Jivraj, Noorallah, Lake Jackson, TX, UNITED STATES
Vanvoorden, Johan, Diepenbeek, BELGIUM
Dixit, Ravi S., Lake Jackson, TX, UNITED STATES
Nicasy, Ruddy, Westerlo, BELGIUM
Gemoets, Frederik E.L., Wommelgem, BELGIUM
PATENT ASSIGNEE(S): Dow Global Technologies Inc. (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003149180	A1	20030807	
	US 6787608	B2	20040907	
APPLICATION INFO.:	US 2002-222273	A1	20020816	(10)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2001-313357P	20010817 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: JENKENS & GILCHRIST, A PROFESSIONAL CORPORATION, 1100

LOUISIANA, SUITE 1800, HOUSTON, TX, 77002-5214
NUMBER OF CLAIMS: 54
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 6 Drawing Page(s)
LINE COUNT: 2300
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to a polyethylene composition with a bimodal molecular weight distribution and articles made therefrom, such as high topload blow moldings and transmission and distribution pipes. The composition comprises a low-molecular-weight (LMW) ethylene homopolymer component and a homogeneous, high-molecular-weight (HMW) ethylene interpolymer component, wherein the LMW component is characterized as having a molecular weight distribution, MWD.sup.L, of less than about 8. The composition is characterized as having a bimodal molecular weight distribution, and a ductile-brittle transition temperature, T.sub.db, of less than -20° C. In some embodiments, the HMW component is characterized by a reverse comonomer distribution.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 14 OF 21 USPATFULL on STN
ACCESSION NUMBER: 97:112415 USPATFULL
TITLE: High activity polyethylene catalysts which produce bimodal or trimodal product molecular weight distributions
INVENTOR(S): Hagerty, Robert O., Metuchen, NJ, United States
Husby, Per K., Somerset, NJ, United States
Kissin, Yury V., East Brunswick, NJ, United States
Mink, Robert I., Warren, NJ, United States
Nowlin, Thomas E., West Windsor, NJ, United States
PATENT ASSIGNEE(S): Mobil Oil Corporation, Fairfax, VA, United States (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 5693583		19971202
APPLICATION INFO.:	US 1997-799086		19970211 (8)

RELATED APPLN. INFO.: Continuation of Ser. No. US 1994-335624, filed on 8 Nov 1994, now abandoned which is a continuation-in-part of Ser. No. US 1993-121821, filed on 15 Sep 1993, now abandoned which is a continuation-in-part of Ser. No. US 1993-8854, filed on 25 Jan 1993, now abandoned which is a continuation of Ser. No. US 1991-712298, filed on 10 Jun 1991, now abandoned

	NUMBER	DATE
PRIORITY INFORMATION:	EP 1992-305256	19920609
	AU 1992-18134	19920610

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Caldarola, Glenn A.
ASSISTANT EXAMINER: Pasterczyk, J.
LEGAL REPRESENTATIVE: Schneller, Marina V., Santini, Dennis P.
NUMBER OF CLAIMS: 28
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 8 Drawing Figure(s); 4 Drawing Page(s)
LINE COUNT: 849
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyst composition for copolymerizing ethylene and alpha-olefins is prepared by treating a silica carrier, in a non-polar hydrocarbon solvent, with a dialkyl magnesium compound, a halogen-containing compound and titanium tetrachloride, to form a catalyst precursor and activating the precursor with dimethylaluminum chloride.

Also disclosed is a process for copolymerizing ethylene and alpha-olefins in the presence of the catalyst of the invention. The polymer products have multimodal molecular weight distributions unlike unimodal molecular weight distributions of polymers prepared with similar catalyst precursors but activated with different alkylaluminum activators, e.g., triethylaluminum or trimethylaluminum.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 15 OF 21 USPATFULL on STN
ACCESSION NUMBER: 97:94307 USPATFULL
TITLE: Process for producing an in situ polyethylene blend
INVENTOR(S): Rifi, Mahmoud R., Kendall Park, NJ, United States
Martino, Carlo F., Somerville, NJ, United States
PATENT ASSIGNEE(S): Union Carbide Chemicals & Plastics Technology Corporation, Danbury, CT, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 5677375		19971014	
APPLICATION INFO.:	US 1996-625612		19960329	(8)

	NUMBER	DATE
PRIORITY INFORMATION:	US 1995-1366P	19950721 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Delmendo, Romulo H.
LEGAL REPRESENTATIVE: Bresch, Saul R.
NUMBER OF CLAIMS: 10
EXEMPLARY CLAIM: 1
LINE COUNT: 951
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A gas phase process for the production of an in situ polyethylene blend comprising contacting ethylene and at least one alpha-olefin comonomer having 3 to 8 carbon atoms with a magnesium/titanium based catalyst system including an activator and a cocatalyst in each of two fluidized bed reactors corrected in series, under polymerization conditions, with the provisos that:

(a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series;

(b) other than the active catalyst referred to in proviso (a) and the cocatalyst referred to in proviso (f), no additional catalyst is introduced into the second reactor;

(c) in the first reactor in which a relatively high molecular weight copolymer is made:

(1) the alpha-olefin is present in a ratio of about 0.01 to about 0.4 mole of alpha-olefin per mole of ethylene; and

(2) optionally, hydrogen is present in a ratio of about 0.001 to about 0.3 moles of hydrogen per mole of ethylene;

(d) in the second reactor in which a relatively low molecular weight copolymer is made:

(1) the alpha-olefin is present in a ratio of about 0.01 to about 0.6 mole of alpha-olefin per mole of ethylene; and

(2) hydrogen is present in a ratio of about 1 to about 2.5 moles of hydrogen per mole of ethylene;

(e) a sufficient amount of one or more hydrocarbons is added to the first reactor or to the mixture formed in the first reactor prior to its introduction into the second reactor to provide about 0.5 to about 15 parts by weight of hydrocarbon(s) per 100 parts by weight of the in situ blend, each of said hydrocarbons being a saturated alicyclic hydrocarbon, which is liquid at process temperature, is non-polar, is essentially amorphous, and contains less than about 15 percent by weight paraffin wax; and

(f) additional hydrocarbyl aluminum cocatalyst is introduced into the second reactor in an amount sufficient to restore the level of activity of the catalyst transferred from the first reactor to about the initial level of activity in the first reactor.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 16 OF 21 USPAT2 on STN

ACCESSION NUMBER:	2007:24522 USPAT2
TITLE:	Bimodal polyethylene composition and articles made therefrom
INVENTOR(S):	Van Dun, Jozef J., Zandhoven, BELGIUM Schouterden, Patrick J. C., Wachtebeke, BELGIUM Sehanobish, Kalyan, Rochester, MI, UNITED STATES van den Berghen, Peter F., Graauw, NETHERLANDS Jivraj, Noorallah, Lake Jackson, TX, UNITED STATES Vanvoorden, Johan, Diepenbeek, BELGIUM Nicasy, Ruddy A. J., Westerlo, BELGIUM Dixit, Ravi S., Lake Jackson, TX, UNITED STATES Gemoets, Frederik E., Wommelgem, BELGIUM
PATENT ASSIGNEE(S):	Dow Global Technologies Inc., Midland, MI, UNITED STATES (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 7345113	B2	20080318	
APPLICATION INFO.:	US 2006-480091		20060630	(11)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2004-817030, filed on 2 Apr 2004, Pat. No. US 7129296 Continuation of Ser. No. US 2002-222273, filed on 16 Aug 2002, Pat. No. US 6787608

	NUMBER	DATE
PRIORITY INFORMATION:	US 2001-313357P	20010817 (60)
	US 2001-313176P	20010817 (60)

DOCUMENT TYPE:	Utility
FILE SEGMENT:	GRANTED
PRIMARY EXAMINER:	Nutter, Nathan M.

NUMBER OF CLAIMS: 13
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 7 Drawing Figure(s); 6 Drawing Page(s)
LINE COUNT: 2153
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to a polyethylene composition with a bimodal molecular weight distribution, methods for making the same, and articles made therefrom, such as high topload blow moldings and transmission and distribution pipes. The composition comprises a low-molecular-weight (LMW) ethylene homopolymer component and a homogeneous, high-molecular-weight (HMW) ethylene interpolymer component, wherein the LMW component is characterized as having a molecular weight distribution, MWD.sup.L, of less than about 8. In some embodiments, the HMW component is characterized by a reverse comonomer distribution.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 17 OF 21 USPAT2 on STN
ACCESSION NUMBER: 2006:41389 USPAT2
TITLE: High strength biomodal polyethylene compositions
INVENTOR(S): Kwalk, Tae Hoon, Belle Mead, NJ, UNITED STATES
PATENT ASSIGNEE(S): Univation Technologies, LLC, Houston, TX, UNITED STATES (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 7193017	B2	20070320	
APPLICATION INFO.:	US 2004-918190		20040813	(10)

DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Nutter, Nathan M.
LEGAL REPRESENTATIVE: Faulkner, Kevin M., Arechederra, Leandro
NUMBER OF CLAIMS: 24
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 1 Drawing Figure(s); 1 Drawing Page(s)
LINE COUNT: 1069
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Disclosed are various compositions, including but not limited to a high strength bimodal polyethylene composition having a density of 0.940 g/cc or more, the composition comprising a high molecular weight polyethylene component having a higher weight average molecular weight (Mw.sub.HMW) and a low molecular weight polyethylene component having a lower weight average molecular weight (Mw.sub.LMW), wherein: the ratio of the higher weight average molecular weight to the lower weight average molecular weight (Mw.sub.HMW:Mw.sub.LMW) is 30 or more; and the composition qualifies as a PE 100 material such that in accordance with ISO 1167 a pipe formed from the composition that is subjected to internal pipe resistance has an extrapolated stress of 10 MPa or more when the internal pipe resistance curve is extrapolated to 50 or 100 years in accordance with ISO 9080:2003(E).

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 18 OF 21 USPAT2 on STN
ACCESSION NUMBER: 2004:335871 USPAT2
TITLE: Multimodal polyolefin pipe
INVENTOR(S): Schramm, Detlef, Sehoenenberg, SWITZERLAND
Quack, Wolfgang, Mettmann, GERMANY, FEDERAL REPUBLIC OF
Damen, Julien, Mettmenstetten, SWITZERLAND

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                          Cham, Pak-Meng, Lake Jackson, TX, UNITED STATES
PATENT ASSIGNEE(S):       Dow Global Technologies, Inc., Midland, MI, UNITED
                          STATES (U.S. corporation)

                               NUMBER        KIND    DATE
                          ---------------- ------ --------
PATENT INFORMATION:       US 7250473         B2   20070731
                          WO 2003020821           20030313
APPLICATION INFO.:        US 2002-484906          20020828  (10)
                          WO 2002-US27503         20020828
                                                  20040810  PCT 371 date

                                 NUMBER        DATE
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PRIORITY INFORMATION:     US 2001-316401P    20010831 (60)
DOCUMENT TYPE:            Utility
FILE SEGMENT:             GRANTED
PRIMARY EXAMINER:         Rabago, Roberto
NUMBER OF CLAIMS:         9
EXEMPLARY CLAIM:          1
LINE COUNT:               708
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB       The present invention relates to a polyethylene resin having a
       multimodal molecular weight distribution, said resin being further
       characterized in that it has a density in the range of from about 0.925
       g/ccm to about 0.950 g/ccm, a melt index (I.sub.2)
       in the range of from about 0.05 g/10 min to about 5 g/10 min, and in
       that it comprises at least one high molecular weight (HMW)
       ethylene interpolymer and at least a low molecular
       weight (LMW) ethylene polymer, and a composition comprising such resin.
       Also provided is a shaped article comprising said resin or composition,
       in particular a pipe.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5   ANSWER 19 OF 21  USPAT2 on STN
ACCESSION NUMBER:         2004:255381  USPAT2
TITLE:                    Bimodal polyethylene pipe composition and article made
                          therefrom
INVENTOR(S):              Van Dun, Jozef J., Missouri City, TX, UNITED STATES
                          Schouterden, Patrick J., Wachtebeke, BELGIUM
                          Sehanobish, Kalyan, Lake Jackson, TX, UNITED STATES
                          van den Berghen, Peter F. M., Graauw, NETHERLANDS
                          Jivraj, Noorallah, Lake Jackson, TX, UNITED STATES
                          Nicasy, Ruddy, Westerlo, BELGIUM
                          Vanvoorden, Johan, Diepenbeek, BELGIUM
                          Dixit, Ravi S., Lake Jackson, TX, UNITED STATES
                          Gemoets, Frederik E., Wommelgem, BELGIUM
PATENT ASSIGNEE(S):       Dow Global Technologies Inc., Midland, MI, UNITED
                          STATES (U.S. corporation)

                               NUMBER        KIND    DATE
                          ---------------- ------ --------
PATENT INFORMATION:       US 7129296         B2   20061031
APPLICATION INFO.:        US 2004-817030          20040402  (10)
RELATED APPLN. INFO.:     Continuation of Ser. No. US 2002-222273, filed on 16
                          Aug 2002, Pat. No. US 6787608

                                 NUMBER        DATE
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PRIORITY INFORMATION: US 2001-313357P 20010817 (60)
DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Nutter, Nathan M.
NUMBER OF CLAIMS: 28
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 7 Drawing Figure(s); 6 Drawing Page(s)
LINE COUNT: 2217
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to a polyethylene composition with a bimodal molecular weight distribution and articles made therefrom. The composition comprises a low-molecular-weight (LMW) ethylene homopolymer component and a homogeneous, high-molecular-weight (LMW) ethylene interpolymer component, wherein the LMW component is characterized as having a molecular weight distribution, MWD.sup.L, of less than about 8. In some embodiments, the HMW component is characterized by a reverse comonomer distribution.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L5 ANSWER 20 OF 21 USPAT2 on STN
ACCESSION NUMBER: 2003:266066 USPAT2
TITLE: High density polyethylene melt blends for improved stress crack resistance in pipe
INVENTOR(S): Harris, Michael G., Findlay, OH, United States
PATENT ASSIGNEE(S): Media Plus, Inc., Findlay, OH, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 6822051	B2	20041123	
APPLICATION INFO.:	US 2002-112200		20020329	(10)

DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Niland, Patrick D.
LEGAL REPRESENTATIVE: Jones Day
NUMBER OF CLAIMS: 46
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 1 Drawing Figure(s); 1 Drawing Page(s)
LINE COUNT: 774
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention provides a polyethylene composition comprising a melt blend of (i) a bimodal high molecular weight high density polyethylene resin having a NCTL stress crack resistance of about 200 hours or greater, and (ii) a high density polyethylene resin selected from the group consisting of a homopolymer high density polyethylene resin, a copolymer high density polyethylene resin, and mixtures thereof, wherein the composition has a minimum NCTL stress crack resistance of 24 hours. In another embodiment, a polyethylene composition comprises a melt blend of the bimodal high molecular weight high density polyethylene resin and a linear low density polyethylene resin. The bimodal high molecular weight high density polyethylene resin can be a commodity film grade resin, the homopolymer and copolymer resins can be milk bottle grade and detergent bottle grade, respectively, and the linear low density polyethylene resin can be a film grade. The compositions are especially useful for manufacture of profile and corrugated pipe and/or pipe fitting applications, and chemical waste applications including sanitary sewer or irrigation piping systems.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

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L5   ANSWER 21 OF 21  USPAT2 on STN
ACCESSION NUMBER:        2003:214537  USPAT2
TITLE:                   Bimodal polyethylene composition and articles made
                         therefrom
INVENTOR(S):             VanDun, Jozef J., Freeport, TX, United States
                         Schouterden, Patrick J., Terneuzen, BELGIUM
                         van den Berghe, Peter F. M., Graauw, NETHERLANDS
                         Nicasy, Ruddy, Tessenderlo, BELGIUM
                         Vanveorden, Johan, Diepenbeek, BELGIUM
                         Gemoets, Frederick E. L., Terneuzen, BELGIUM
                         Sehanobish, Kalyan, Lake Jackson, TX, United States
                         Jivraj, Noorallah, Lake Jackson, TX, United States
                         Dixit, Ravi S., Lake Jackson, TX, United States
PATENT ASSIGNEE(S):      Dow Global Technologies, Inc., Midland, MI, United
                         States (U.S. corporation)

                              NUMBER       KIND    DATE
                         --------------- ------ --------
PATENT INFORMATION:      US 6787608        B2   20040907
APPLICATION INFO.:       US 2002-222273         20020816  (10)

                                NUMBER        DATE
                         ----------------- --------
PRIORITY INFORMATION:    US 2001-313357P    20010817 (60)
DOCUMENT TYPE:           Utility
FILE SEGMENT:            GRANTED
PRIMARY EXAMINER:        Nutter, Nathan M.
NUMBER OF CLAIMS:        52
EXEMPLARY CLAIM:         1
NUMBER OF DRAWINGS:      7 Drawing Figure(s); 6 Drawing Page(s)
LINE COUNT:              2038
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB       The invention relates to a polyethylene composition with a bimodal
         molecular weight distribution and articles made therefrom, such as high
         topload blow moldings and transmission and distribution pipes. The
         composition comprises a low-molecular-weight (LMW) ethylene homopolymer
         component and a homogeneous, high-molecular-weight (HMW)
         ethylene interpolymer component, wherein the LMW
         component is characterized as having a molecular weight distribution,
         MWD.sup.L, of less than about 8. The composition is characterized as
         having a bimodal molecular weight distribution, and a ductile-brittle
         transition temperature, T.sub.db, of less than -20° C. In some
         embodiments, the HMW component is characterized by a reverse comonomer
         distribution.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.


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L5   ANSWER 20 OF 21  USPAT2 on STN
ACCESSION NUMBER:        2003:266066  USPAT2
TITLE:                   High density polyethylene melt blends for improved
                         stress crack resistance in pipe
INVENTOR(S):             Harris, Michael G., Findlay, OH, United States
PATENT ASSIGNEE(S):      Media Plus, Inc., Findlay, OH, United States (U.S.
                         corporation)

                              NUMBER       KIND    DATE
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PATENT INFORMATION:	US 6822051	B2	20041123	
APPLICATION INFO.:	US 2002-112200		20020329	(10)
DOCUMENT TYPE:	Utility			
FILE SEGMENT:	GRANTED			
PRIMARY EXAMINER:	Niland, Patrick D.			
LEGAL REPRESENTATIVE:	Jones Day			
NUMBER OF CLAIMS:	46			
EXEMPLARY CLAIM:	1			
NUMBER OF DRAWINGS:	1 Drawing Figure(s); 1 Drawing Page(s)			
LINE COUNT:	774			

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM The Departments of Transportation (DOT) of many states of the United States require plastic pipe used for DOT projects to meet American Association of State Highway Transportation Officials (AASHTO) standards that include American Society of Testing Materials (ASTM) standards. Historically, corrugated pipe manufacturers used monomodal medium molecular weight (MMW)-HDPE to meet the required cell classifications in ASTM D-3350 for melt index, density, flexural modulus, tensile strength, bent strip environmental stress crack resistance (ESCR) and notched izod. The modality of the polymer (e.g., monomodal, bimodal, trimodal, and the like) relates to the number of peaks in a molecular weight distribution curve. In some cases, blends of virgin, recycled, reprocessed and/or scrap polyethylenes were used to achieve the required properties for specific cell classifications. Although these methods were effective for satisfactory short-term physical properties of the resulting pipe, in the longer term in the field the pipe had poor slow crack growth properties.

SUMM In an attempt to lower costs and still meet the required standards for HDPE pipe compositions, melt blends of lower priced commodity grades of HDPE were prepared in two- and three-material blend combinations and then tested for the cell classification properties. For example, monomodal high molecular weight (HMW)-HDPE copolymers, such as those used for blow-molded 55 gallon drums, were melt blended with monomodal MMW-HDPE copolymers, such as those used for blow-molded detergent bottles. However, the resulting HDPE blend had NCTL values that were less than 24 hours, although the melt index, density, notched izod, flexural modulus and tensile strength were within the AASHTO specifications. Therefore, this attempt was not successful in providing a viable substitute for the high cost specialty resins for profile and corrugated pipe applications.

DETD The Flow Rate Ratio (FRR), such as that defined in ASTM D1238 is a good indicator of the weight average molecular weight and a generally accepted test method for the polydispersity of polyethylene resin grades. Polydispersity is the ratio of the weight average molecular weight to the number average molecular weight, and the lower the polydispersity (and the FRR), the narrower is the MWD. The FRR is the ratio of the high load melt index (HLMI, condition F at 21.6 kg at 190° C.) to the melt index (MI, condition E at 2.16 kg and 190° C.). It is preferred that the FRR of the bimodal HMW-HDPE resins for use in the invention compositions is less than 200.

DETD Copolymer MMW-HDPE resins suitable for use in the invention compositions can have a density of about 0.941 to about 0.958 g/cm.sup.3 and a melt flow index of about 0.01 to about 1.5. The copolymer HDPE comprises ethylene monomers and another monomer that can be propylene, butene, hexene, octene, metallocene, or the like, as is known

to those skilled in the art. Typical copolymer MMW-HDPE resins are commercially available for applications such as detergent and bleach bottles. The resins can be virgin resins or can be recycled, reprocessed or scrap resins. The NCTL values for these resins are determined prior to using them as components in the invention compositions. The NCTL value for a commodity copolymer is less than 24 hours, typically about five to about ten hours. These resins are usually identified by a generic number grade of "5502" designating detergent bottle grade. Virgin copolymer MMW-HDPE resins suitable for use in the invention compositions are generally available from the same companies listed above for the homopolymer MMW-HDPE resins.

DETD The amount of the bimodal HMW-HDPE resin in combination with the homopolymer MMW-HDPE resin and/or the copolymer MMW-HDPE resin, or the amount of the bimodal HMW-HDPE resin in combination with the LLDPE resin in the composition can vary depending on the NCTL values for each of the resins, as well as the desired density and melt flow index properties of the melt blended composition. The density and melt flow index values of the virgin resins are often provided by the manufacturer. Recycled films, reprocessed, reworked and scrap materials can be tested for density, melt index, tensile strength notched izod and NCTL values by known methods described above, and blended in the proper proportions to achieve the desired properties of the composition without undue experimentation, as known to those of ordinary skill in the art. In addition to altering the ratios of the ingredients to achieve specific physical properties of the composition, the ratios of the ingredients can be determined to achieve desirable processing characteristics, such as for a given extrusion process or a pipe profile design. For example, the melt flow index, which is a measure of the viscosity of the component, affects the processability of the melt blend. The lower the melt flow index, the higher the viscosity of the component. The melt flow index is a general indicator of the weight average molecular weight of the resins.

DETD The FRR, described above, is also a good indicator of the processability at higher shear rates of the final melt blended compound. Therefore, an advantage of the methods of the invention, is that the FRR of a final composition can be predetermined by selecting resins having FRR values that will achieve desired processing and final product considerations, such as processability, melt strength, die swell ratio , forming, wall thickness, and the like. It is preferred that the final melt-blended composition have an FRR of about 80 to about 125, with about 90 to about 110 being more preferred. It has been found that melt-blended compositions with FRR greater than 150 risk failing the 24 hour stress crack resistance test (NCTL) and may be difficult to process into a molded article.

DETD The bimodal HMW-HDPE employed in Example 1 was melt blended in a ratio of 35:65 with a copolymer MMW-HDPE (Equistar "5502", Lot LR734) having a NCTL=8.0 hours, by the method described in Example 1. The copolymer MMW-HDPE had the following properties: MI=0.35, density=0.954 and notched izod=3.0. The properties of the resulting high density polyethylene composition are illustrated in Table 1.

DETD The bimodal HMW-HDPE employed in Examples 1 and 2 was melt blended in a ratio of 80:20 with a LLDPE having a NCTL of 1500 hours, by the method described in Example 1. The LLPDE had the following properties: MI=0.50, density=0.925, notched izod=15. The properties of the resulting polyethylene composition are illustrated in Table 1.

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L5 ANSWER 19 OF 21 USPAT2 on STN

S/N 10/568,739

ACCESSION NUMBER: 2004:255381 USPAT2
TITLE: Bimodal polyethylene pipe composition and article made therefrom
INVENTOR(S): Van Dun, Jozef J., Missouri City, TX, UNITED STATES
Schouterden, Patrick J., Wachtebeke, BELGIUM
Sehanobish, Kalyan, Lake Jackson, TX, UNITED STATES
van den Berghen, Peter F. M., Graauw, NETHERLANDS
Jivraj, Noorallah, Lake Jackson, TX, UNITED STATES
Nicasy, Ruddy, Westerlo, BELGIUM
Vanvoorden, Johan, Diepenbeek, BELGIUM
Dixit, Ravi S., Lake Jackson, TX, UNITED STATES
Gemoets, Frederik E., Wommelgem, BELGIUM
PATENT ASSIGNEE(S): Dow Global Technologies Inc., Midland, MI, UNITED STATES (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 7129296	B2	20061031
APPLICATION INFO.:	US 2004-817030		20040402 (10)

RELATED APPLN. INFO.: Continuation of Ser. No. US 2002-222273, filed on 16 Aug 2002, Pat. No. US 6787608

	NUMBER	DATE
PRIORITY INFORMATION:	US 2001-313357P	20010817 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Nutter, Nathan M.
NUMBER OF CLAIMS: 28
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 7 Drawing Figure(s); 6 Drawing Page(s)
LINE COUNT: 2217
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to a polyethylene composition with a bimodal molecular weight distribution and articles made therefrom. The composition comprises a low-molecular-weight (LMW) ethylene homopolymer component and a homogeneous, high-molecular-weight (LMW) ethylene interpolymer component, wherein the LMW component is characterized as having a molecular weight distribution, MWD.sup.L, of less than about 8. In some embodiments, the HMW component is characterized by a reverse comonomer distribution.

SUMM We have discovered a bimodal high density polyethylene composition that exhibits improved durability. The new composition comprises at least a low-molecular-weight (LMW) ethylene homopolymer component having a molecular weight distribution, MWD.sub.L, of less than about 8 and a high-molecular-weight (HMW) ethylene interpolymer component. Some composition are characterized as having a bimodal molecular weight distribution and a ductile-brittle transition temperature, T.sub.db, of less than -20° C. Preferably, the overall M.sub.w/M.sub.n (indicative of the molecular weight distribution or MWD) of the novel composition is relatively narrow, and the M.sub.w/M.sub.n of the LMW component is relatively narrow, or the MWD for both the LMW component and the HMW component is also relatively narrow, or the MWD of the each component is relatively narrow and completely distinct from one another. In some embodiments, the HMW component is characterized by a "reverse comonomer distribution."

DETD Embodiments of the invention provide a new polyethylene composition which can be used for making water or oil pipes and other products. The new composition comprises a low-molecular-weight (LMW) ethylene

homopolymer component and a high-molecular-weight (HMW) ethylene interpolymer component. The new composition is characterized by a relatively narrow bimodal molecular weight distribution. The bimodality of the molecular weight distribution of the new composition is due to the difference in the MWD of the LMW component and the HMW component. Preferably, the MWD of the LMW and HMW components individually is unimodal but is different and distinct from each other such that, when mixed, the resulting composition has an overall bimodal molecular weight distribution. The LMW ethylene homopolymer component has a molecular weight distribution, MWD.sup.L, of less than about 8. In some enbodiments, the new composition is characterized as having a ductile-brittle transition temperature, T.sub.db, of less than -20° C. In some embodiments, the HMW component is characterized by a substantially uniform comonomer distribution or a reverse comonomer distribution.

DETD The term "interpolymer" is used herein to indicate, for example, a copolymer or a terpolymer. That is, at least one other comonomer is polymerized with ethylene to make an interpolymer.

DETD The relatively narrow molecular weight distribution, bimodal polyethylene composition is also characterized as having an overall density of greater than or equal to 0.94 g/cm.sup.3, preferably in the range of from about 0.94 to about 0.97 g/cm.sup.3, more preferably from about 0.948 to about 0.968 g/cm.sup.3, and an I.sub.5 melt index of less than or equal to 0.5 g/10 min., preferably in the range of from about 0.01 to about 0.5 g/10 minutes, more preferably from about 0.05 to about 0.45 g/10 minutes.

DETD Generally, the novel composition may comprise any amount of the LMW component or the HMW component, i.e., either component can be present from about 0.5 weight percent to about 99.5 percent. In some embodiments, the novel composition comprises from about 35 to about 65 weight percent, preferably from about 45 to about 55 weight percent of a low molecular weight (LMW) high density ethylene homopolymer component. The LMW component has an I.sub.2 melt index of less than or equal to 2000 g/10 minutes, preferably it is characterized as having an I2 melt index of from about 30 to about 2000 g/10 minutes, more preferably 40 to 1000 g/10 min., most preferably from about 50 to about 150 g/10 minutes. The M.sub.w of the LMW component is preferably in the range from about 10,000 to about 40,000 g/mole, more preferably in the range of from about 25,000 to about 31,000 g/mole. The M.sub.w/M.sub.n of the LMW component is preferably less than 8, more preferably less than 5, most preferably about 3 or less. In other embodiments the M.sub.w/M.sub.n of the LMW component is about 2 or less. In some embodiments, the molecular weight distribution, M.sub.w/M.sub.n, of the LMW component is in the range of from about 1.5 to about 4.8. In certain embodiments, the M.sub.w/M.sub.n of the LMW component is most preferably in the range of from about 3.2 to about 4.5. The density of the LMW component is preferably greater than 0.960 g/cm.sup.3, more preferably greater than or equal to 0.965 g/cm.sup.3 and most preferably greater than or equal to 0.970 g/cm.sup.3.

DETD The novel composition comprises from about 65 to about 35 weight percent, more preferably from about 55 to about 45 weight percent of a high molecular weight (HMW) ethylene interpolymer component. The HMW interpolymer component has an I.sub.2 melt index of less than or equal to 0.1 g/10 minutes, preferably it is characterized as having an I.sub.2 melt index of from about 0.001 to about 0.1 g/10 minutes, more preferably from about 0.005 to about 0.05 g/10 minutes, most preferably from about 0.0085 to about 0.016. The HMW component is also characterized by its I.sub.21.6 melt index ranging from about 0.1 to about 1.0 g/10 min. In some embodiments, I.sub.21.6 preferably ranges from about 0.1 to

about 0.6 g/10 min., preferably from about 0.1 to about 0.5 g/10 min., more preferably from about 0.3 to about 0.4 g/10 min. In other embodiments, I.sub.21.6 ranges from greater than 0.6 to about 1.0 g/10 min., preferably from about 0.65 to about 0.95 g/10 min., more preferably from about 0.7 to about 0.9 g/10 min.

DETD In other embodiments, the HMW interpolymer component is a homogeneous polymer or is characterized as having a substantially uniform comonomer distribution. Information regarding the relative uniformity of the comonomer distribution for ethylene interpolymers is typically described by the SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index), which are used interchangeably herein. SCBDI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content and represents a comparison of the comonomer distribution in the interpolymer to the comonomer distribution expected for a Bemoullian distribution. The SCBDI of an interpolymer can be readily calculated from TREF as described, for example, by Wild et al., Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982); U.S. Pat. No. 4,798,081; U.S. Pat. No. 5,008,204; or L. D. Cady, "The Role of Comonomer Type and Distribution in LLDPE Product Performance," SPE Regional Technical Conference, Quaker Square Hilton, Akron, Ohio, 1-2, pp. 107-119 (1985), the disclosures of all four of which are incorporated herein by reference.

DETD Processes for preparing homogeneous polymers are disclosed in U.S. Pat. Nos. 5,206,075, 5,241,031, and PCT International Application WO 93/03093, each of which is hereby incorporated by reference thereto in its entirety. Further details regarding the production and use of one genus of homogeneous ethylene α-olefin copolymers are disclosed in U.S. Pat. No. 5,206,075, to Hodgson, Jr.; U.S. Pat. No. 5,241,031, to Mehta; PCT International Publication Number WO 93/03093, in the name of Exxon Chemical Company; PCT International Publication Number WO 90/03414, in the name of Exxon Chemical Patents, Inc., all four of which are hereby incorporated in their entireties, by reference there. Still another genus of homogeneous ethylene/α-olefin copolymers is disclosed in U.S. Pat. No. 5,272,236, to Lai, et. al., and U.S. Pat. No. 5,278,272, to Lai, et. al., both of which are hereby incorporated in their entireties, by reference thereto.

DETD Homogeneously branched linear ethylene/α-olefin interpolymers may also be prepared using polymerization processes (for example, as described by Elston in U.S. Pat. No. 3,645,992) which provide a homogeneous short chain branching distribution. In his polymerization process, Elston uses soluble vanadium catalyst systems to make such polymers. However, others such as Mitsui Petrochemical Company and Exxon Chemical Company have used so-called single site catalyst systems to make polymers having a homogeneous linear structure. U.S. Pat. No. 4,937,299 to Ewen et al. and U.S. Pat. No. 5,218,07 1, to Tsutsui et al. disclose the use of catalyst systems based on hafnium for the preparation of homogeneous linear ethylene polymers. Homogeneous linear ethylene/α-olefin interpolymers are currently available from Mitsui Petrochemical Company under the trade name "Tafmer" and from Exxon Chemical Company under the trade name "Exact".

DETD Substantially linear ethylene/α-olefin interpolymers are available from The Dow Chemical Company as AFFINITY.TM. polyolefin plastomers. Substantially linear ethylene/α-olefin interpolymers may be prepared in accordance with the techniques described in U.S. Pat. Nos. 5,272,236, 5,278,272, and 5,665,800, which are hereby incorporated by reference.

DETD In yet other embodiments, the HMW ethylene

interpolymer component, is characterized as having a reverse comonomer distribution such that a higher amount of comonomer in the interpolymer component is incorporated in the high molecular weight fractions of the interpolymer component. That is, the polymer fractions having a M.sub.w greater than or equal to the average M.sub.w of the interpolymer component are characterized as having a higher weight average amount of comonomer than the polymer fractions having a M.sub.w less than the average M.sub.w of the interpolymer component. For example, in some embodiments, the total molar comonomer content of all polymer fractions having a M.sub.w greater than or equal to 300,000 g/mole will be at least 25 percent higher, more preferably at least 30 percent higher than the molar comonomer content of those polymer fractions having a Mw of less than or equal to 100,000 g/mole.

DETD Reverse comonomer distribution may be quantified as follows. With respect to ethylene copolymer component, when, in cross fractionation chromatography (CFC) of the ethylene copolymer, with respect to extraction at an arbitrary temperature T(° C.) falling within the range of between a first temperature at which a maximum amount of extraction is exhibited and a second temperature which is the lower temperature of either the temperature of 10° C. higher than said first temperature of 96° C., the relationship between the arbitrary temperature T(° C.) and a point in molecular weight on a molecular weight distribution profile of a copolymer fraction extracted at the arbitrary temperature T(° C.) at which point in molecular weight the molecular weight distribution profile of the copolymer fraction shows a peak having a maximum intensity is treated by the least squares method to obtain an approximate straight line within the range of between said first temperature and said second temperature; if there is the copolymer fraction the amount of which is less than 1% by weight on the total amount, excluding purge, of copolymer fraction extracted at temperatures in the overall range of extraction temperatures in CFC, the copolymer fraction can be excluded from the calculation for the approximate straight line; the approximate straight line has a gradient within the range defined by the formula (I): -1≤{log Mp(T.sup.1)-log Mp(T.sup.2)}/(T.sup.1-T.sup.2)≤0.005 (I) wherein:

DETD With respect to conventional ethylene copolymers produced using a conventional Ziegler catalyst, the gradient {log Mp(T.sup.1)-log Mp(T.sup.2)}/(T.sup.1-T.sup.2) is generally a positive value. With respect to conventional ethylene copolymers produced using conventional metallocene catalysts which have recently been being put into practical use, the gradient {log Mp(T.sup.1)-log Mp(T.sup.2)}/(T.sup.1-T.sup.2) is almost 0, thus they have a substantially uniform comonomer distribution.

DETD The ethylene copolymer component in some embodiments of the invention has a gradient [{log Mp(T.sup.1)-log Mp(T.sup.2)}/(T.sup.1-T.sup.2)] which is relatively large in negative value (within the range of from -0.005 to -1). This indicates that the copolymer has a reverse comonomer distribution. In other words, in the ethylene copolymer component, a copolymer fraction having a high comonomer content has a high molecular weight, contrary to the conventional ethylene copolymers, in which a copolymer fraction having a high comonomer content typically has a low molecular weight.

DETD In other embodiments, with respect to the ethylene copolymer component, the amount of such copolymer fractions extracted at temperatures which are at least 10° C. lower than the first temperature as defined above are relatively small. Specifically, when the ethylene copolymer component is measured by CFC, the ethylene copolymer shows

characteristics such that the sum of respective amounts of copolymer fractions extracted at temperatures which are at least 10° C. lower than the first temperature as defined above is 8% by weight or less, preferably 5% by weight or less, more preferably 3.5% by weight or less, based on the total amount of copolymer fractions extracted at temperatures in the overall range of extraction temperatures in CFC, but excluding the purge.

DETD In some embodiments, certain fractions of the ethylene copolymer component satisfy the following formula (II): log(Mt)-log(Mc)≤0.5 (II) wherein Mt is a point in molecular weight on a molecular weight distribution profile at which the profile shows a peak having a maximum intensity, and Mc is an arbitrary point in molecular weight on the molecular weight distribution profile.

DETD The molecular weight distribution profile is obtained together with a comonomer content distribution profile by subjecting the ethylene copolymer to gel permeation chromatography-Fourier transformation infrared spectroscopy (GPC/FT-IR). An approximate straight line is obtained from the comonomer content distribution profile by the least squares method. The line has a gradient (hereinafter "comonomer distribution gradient") defined by the formula (III): {C(Mc.sup.1)-C(Mc.sup.2)}/(log Mc.sup.1-log Mc.sup.2) (III) wherein:

DETD As mentioned above, the molecular weight distribution profile and the comonomer content distribution profile can be obtained by subjecting the ethylene copolymer to gel permeation chromatography/Fourier transformation infrared spectroscopy (GPC/FT-IR). For example, the measurement by GPC is conducted using 150C ALC/GPC (manufactured and sold by Waters Assoc. Co. U.S.A.), in which three columns [one Shodex At-807S (manufactured and sold by Showa Denko K. K., Japan) and two TSK-gel GMH-H6 (manufactured and sold by Tosoh Corp., Japan)], which are connected in series, are used, and the measurement by FT-IR is connected by dissolving 20 to 30 mg of a sample in 15 ml of trichlorobenzene having a temperature of 140° C., and applying 500 to 1,000 μl of the resultant solution to a FT-IR apparatus (PERKIN-ELMER 1760X, manufactured and sold by Perkin Elmer Cetus, Co., Ltd., U.S.A.).

DETD The novel composition can be made by a variety of methods. For example, it may be made by blending or mixing a LMW high density homopolyethylene component and a HMW ethylene copolymer component. Alternatively, it may be made in a plurality of polymerization reactors.

DETD The HMW interpolymer component comprises ethylene with at least one olefin, preferably a C.sub.3-C.sub.20 α-olefin or C.sub.4-C.sub.18 diolefin. Suitable comonomers include, but are not limited to, the C.sub.3-C.sub.20 α-olefin, such as propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene. In some embodiments, the HMW interpolymer component is a copolymer of ethylene and 1-butene. Chain transfer agents can also be used in the polymerization.

DETD Density is measured in accordance with ASTM D-792. Melt index measurements are performed according to ASTM D-1238, Condition 190° C./2.16 kilogram (kg) and Condition 190° C./5 kg, and are known as I.sub.2 and I.sub.5, respectively. Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. Melt index is reported as g/10 minutes. Melt index determinations can also be performed with even higher weights, such as in accordance with ASTM D-1238, Condition 190° C./10 kg and Condition 190° C./21.6 kg, and are known

as I.sub.10 and I.sub.21.6, respectively.

DETD The term "melt flow ratio" is used herein in the conventional sense as the ratio of a higher weight melt index determination to a lower weight determination. For measured I.sub.10 and I.sub.2 melt index values, the melt flow ratio is conveniently designated as I.sub.10/I.sub.2. For I.sub.21.6 and I.sub.10 values, the ratio is designated I.sub.21.6/I.sub.10.

DETD Generally for a multilayer film structure, the novel compositions described herein comprise at least one layer of the total multilayer film structure. Other layers of the multilayer structure include but are not limited to barrier layers, and/or tie layers, and/or structural layers. Various materials can be used for these layers, with some of them being used as more than one layer in the same film structure. Some of these materials include: foil, nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, LLDPE, HDPE, LDPE, nylon, graft adhesive polymers (e.g., maleic anhydride grafted polyethylene), and paper. Generally, the multilayer film structures comprise from 2 to about 7 layers.

DETD The small pilot slurry dual reactors had a volume of 10 liter and were operated at a liquid level of about 70% (by volume) and agitated at 1000 rpm using a Lightnin A310 mixing blade. The reactor temperature was kept constant by jacket cooling and the melt index was controlled via hydrogen addition while density was controlled via comonomer addition wherein the comonomer was 1-butene in all cases. All feed streams were fed through dip pipe legs in the liquid phase to allow intimate mixing. The diluent was hexane.

DETD Inventive Example 1 was prepared by melt-compounding Examples 1A and 1B with 750 ppm calcium stearate and 3000 ppm Irganox.TM. B225 on a LEISTRITZ ZSE 60 counter-rotating twin screw extruder. Included in the melt-compounding was a carbon black masterbatch based on DOWLEX.TM. LLDPE 2384 resin to provide a final carbon black concentration of 2.28 weight percent. The melt-compounding was mild in that the extruder (65 mm, L/D 24) was operated using a temperature profile of 190 to 220° C. at 28 kg/hr and 40 rpm. Inventive Example 1 was fed to achieve a minimal specific energy and the atmosphere on the powder feeder was controlled to be 1-4% oxygen by using a nitrogen purge in the feeding chute. Inventive Example 1 was extruded two times to ensure good homogeneity. Final product properties for Inventive Example 1 can be found in Table 4. Its I.sub.5 melt index was 0.27 g/10 minutes and its density was 0.9668 g/cm.sup.3.

DETD As described in Tables 4-7, Inventive Example 2 was produced in a manner similar to Inventive Example 1, except Inventive Example 2 did not require blending of duplicative runs to increase available quantities. Inventive Example 2 was stabilized and compounded with carbon black in manner similar to Inventive Example 1 and, as described in Table 7, had an I.sub.5 melt index of 0.20 g/10 minutes and a density of 0.9604 g/cm.sup.3.

DETD As described in Tables 4-6, for Inventive Example 3, which consisted of melt-compounding three substantially equivalent polymerization runs to provide sufficient quantities (i.e., Examples 3a, 3b and 3c), each run was conducted in a manner similar to that described above for Inventive Example 1. Inventive Example 3 was stabilized and compounded with carbon black in manner similar to Inventive Example 1 and, as described in Table 7, had an I.sub.5 melt index of 0.42 g/10 minutes and a density of 0.9640 g/cm.sup.3. As described in Tables 4-6,

for Inventive Example 4, which consisted of dry blending two substantially equivalent polymerization runs to provide sufficient quantities (i.e., Examples 4a and 4b), each run was conducted in a manner similar to that described above for Inventive Example 1. Inventive Example 4 was stabilized and compounded with carbon black in manner similar to Inventive Example 1 and, as described in Table 7, had an I.sub.5 melt index of 0.41 g/10 minutes and a density of 0.9611 g/cm.sup.3.

DETD Comparative run 1 consisted of HOSTALEN CRP 100, supplied commercially by BASELL as a PE100 pressure pipe resin. Comparative run 1 had an I.sub.5 melt index of 0.21 g/10 minutes and a density of 0.9640 g/cm.sup.3 and is recognized in the pressure pipe industry as the PE100 resin with the highest hydrostatic strength. HOSTALEN CRP 100 is manufactured exclusively with Ziegler-Natta catalyst in a dual reactor system.

DETD Comparative run 2 consisted of a HDPE PE100 pressure pipe resin. Comparative run 2 had an I.sub.5 melt index of 0.40 g/10 minutes and a density of 0.9593 g/m.sup.3. Like CRP 100, this resin is manufactured using a conventional Ziegler-Natta catalyst system. Differential scanning calorimetry analysis was performed using a Seiko DSC to determine crystallinity and peak melting point.

DETD
TABLE 11

Product and Performance Properties of Inventive Examples

		Inventive Example		
		2	5	6
Melt-Index				
I.sub.5	g/10 min	0.21	0.25	0.25
I.sub.21.6	g/10 min	4.71	5.04	6.31
I.sub.21.6/I.sub.5		22.43	20.16	25.24
Density	g/cm.sup.3	0.9511	0.9508	0.9508
Butene (FTIR)	mole %	0.53	0.45	ND
GPC				
M.sub.w		229900	223100	201400
M.sub.n		13213	15200	15700
M.sub.w/M.sub.n		17.4	14.68	12.83
M.sub.z			832600	727200
RCD (Fractionation)		Yes	Yes	Yes
Calcium Stearate	ppm		680	
Irganox .TM. 1010	ppm	2080	845	329
Irgafos .TM. 168 total	ppm	2691		1900
Irgafos .TM. 168 remaining	ppm	2784	2000	1723
DSC				
T.sub.o	° C.	122.2	122.1	121.2
T.sub.m	° C.	133.2	134.4	133.1
Crystallinity	%	72.77	68.11	69.0
OIT ° C.	min.	66	46	50
PENT	min.	>464484	>179796	>150000
G.sub.c Brittle Ductile, ° C.				
40	kJ/m.sup.2			
23	kJ/m.sup.2	33	36.7.sup.d	39.8.sup.d
0	kJ/m.sup.2			
-5				
-10	kJ/m.sup.2		21.5.sup.d	23.2.sup.d

-20	kJ/m.sup.2	18.4	17.7.sup.d	21.0.sup.d
-30	kJ/m.sup.2		17.1.sup.d	17.4.sup.d
-40	kJ/m.sup.2		14.5.sup.d	17.1.sup.d
-50	kJ/m.sup.2		13.6.sup.d	12.5.sup.b
-60	kJ/m.sup.2		12.8.sup.b	12.0.sup.b
IZOD	kJ/m.sup.2	545	44.6	44.7
Tensile properties				
Yield stress	MPa	23.1	23.7	24.8
Yield strain	%	11.7	10.6	11.0
Break stress	MPa	36.6	42.4	42.2
Ultimate tensile stress	MPa	36.6	42.4	42.2
Elongation	%	673	683	697
Secant modulus	MPa	556	622	614
Young's modulus	MPa	954	1044	957
3 point flex. modulus	MPa	831	918	983
Rheology				
viscosity @ .1/s		88371	86924	81283
viscosity @ 100/s		3100	2879	2680
Power law k		37311	35654	34597
Power law N		0.50565	0.4972	0.4747
Melt-Tension				
Screw	rpm		27.9	27.0
Pressure	Bar		107	115
V.sub.o	cm/sec		3.1	3.2
V.sub.z	cm/sec		46.0	53
M.sub.e			13.84	15.56
Force	cN		44.0	38.0
T.sub.z	cN/sec		8225	8675
Swell	%		127	122

.sup.bindicates brittle failure mode observed;
.sup.dindicates ductile failure mode observed.

DETD For Inventive Example 7, the polymerization was conducted continuously in a first continuously stirred autoclave tank reactor (CSTR), operating at a liquid volume of 130 liter of hexane diluent. The catalyst was injected as a slurry using hexane as carrier into the liquid of the reactor. The reactor was controlled at a constant liquid temperature by circulation of cold water in the cooling jacket of the reactor. Hexane, ethylene and hydrogen were fed to this first reactor. The melt index of the powder produced in the reactor was controlled by the hydrogen flow rate. The liquid volume of 130 liter was controlled by transferring slurry from the first reactor to a stripper.

DETD The second reactor was controlled at a temperature of 70° C. by circulation of cold water in the cooling jacket of the reactor. Ethylene was fed to the second reactor to control the split and butene as comonomer was fed to the second reactor to control the density of the product. The same catalyst system as was fed to the first reactor was also separately fed to the second reactor. The melt index of the product produced in the second reactor was controlled by controlling the hydrogen concentration in the reactor by continuous venting of the gas phase of the reactor. The liquid volume of 180 liter was controlled by discontinuously transferring slurry from the second reactor to a fluidized bed drier, where powder product was separated from the liquid and unreacted monomers. The powder product was

further dried using a rotary drier to obtain a dry powder product. The run conditions are listed in Table 12.

DETD In this evaluation, melt index and melt index ratios were determined according to ASTM D-1238; the comonomer content was measured using Fourier Transform Infra Red (FTIR); the molecular weight distributions were measured using high temperature GPC; slow crack growth performance was assessed using PENT lifetime (Pennsylvania Notch Test); critical strain energy release rate, or G.sub.c, was determined as described above; and viscosity was measured using a Bohlin Constant Stress Rheometer in the oscillatory mode at 190° C. wherein angular velocities were varied from 0.1 rad/s to 100 rad/s. The viscosity at 100 rad/s is representative for the processability of the resin on fabrication equipment: the lower the viscosity, the easier the processability will be. The viscosity at 0.1 rad/s is proportional to the melt strength of the material. The ratio of these two viscosities also gives an indication of the shear sensitivity of the material. The various properties of Inventive Examples 7 and 8, as compared to comparative run 2, are presented in Table 13.

DETD

TABLE 13

Product properties

		Inventive Example 7	Inventive Example 8	comparative run 2
Melt index				
I.sub.5	g/10 min	0.21	0.17	0.40
I.sub.10	g/10 min	0.79	0.66	
I.sub.21.6	g/10 min	5.72	4.87	9.39
Ratio I.sub.21.6/I.sub.5	--	27.24	28.65	22.70
Density	g/cm.sup.3	0.951	0.9493	0.9593
Comonomer	mole %	0.45	0.55	
GPC Results	M.sub.w	226400	246800	
	M.sub.w/M.sub.n	15.61	15.14	
RCD		Yes	Yes	No
Rheology				
Viscosity @.1/s	Pa .multidot. s	95622	109292	60703
Viscosity @100/s	Pa .multidot. s	2758	2860	2338
Tensile properties				
Yield stress	MPa	24.25	24.09	23.08
Tens Young's Modulus	MPa	1013	1002	986
Flex Young's Modulus	MPa	1014	921	
G.sub.c Brittle Ductile				
40° C.	kJ/m.sup.2	45.5.sup.d	48.5.sup.d	
23° C.	kJ/m.sup.2	36.6.sup.d	43.6.sup.d	11
0° C.	kJ/m.sup.2	26.9.sup.d	29.2.sup.d	
-10° C.	kJ/m.sup.2	23.3.sup.d	25.8.sup.d	
-20° C.	kJ/m.sup.2	22.1.sup.d	22.7.sup.d	
-30° C.	kJ/m.sup.2	19.sup.d	20.5.sup.d	
-50° C.	kJ/m.sup.2	19.1.sup.d	20.3.sup.d	
-60° C.	kJ/m.sup.2	14.sup.b	14.8.sup.b	
-70° C.	kJ/m.sup.2	13.2.sup.b	13.7.sup.b	
Pent [SCG]	minutes	>142338	>200000	>10000

.sup.bindicated brittle failure mode observed

DETD In another evaluation, the effect of providing a narrow MWD for the higher molecular weight, lower density component was investigated. Comparative run 3 was prepared using the single reactor continuously

stirred-tank slurry polymerization with a Ziegler-Natta catalyst system. The catalyst was a non-decanted alkoxide (NDA) and the product was produced under process conditions presented in Table 15. The resulting high density product had an I.sub.2 melt index of 94 g/10 minutes and a density of 0.9719 g/cm.sup.3 and was produced at a total pressure of 12 bars, a hexane feed rate of 1500 g/hr of hexane, an ethylene supply rate of 816 g/hr ethylene and a hydrogen fed rate of 140 Nliters/hr and the reactor was operated at an average residence time of 82 minutes.

DETD Comparative run 4 was prepared with the same catalyst system as comparative run 3 using different process conditions as presented in Table 17. Comparative run 4 was an ethylene/1-butene copolymer and had an I21.6 melt index (Condition 190° C., 21.6 kg) of 0.38 g/10 minutes and a density of 0.9306 g/cm.sup.3. Comparative run 4 was produced at a total pressure of 12 bars, a hexane feed rate of 2800 g/hr, an ethylene supply rate of 856 g/h, a hydrogen supply rate of 7.2 Nl/h and a butene supply rate of 200 g/hr and the reactor was operated at an average residence time of 48 minutes.

DETD Comparative run 5 was a product sample taken immediately after the first reactor of a two-reactor slurry polymerization system. Comparative run 5 was a high density product, low molecular weight product and had an I.sub.2 melt index of 118 g/10 minutes and a density of 0.9720 g/cm.sup.3.

DETD Comparative run 6 was produced using a supported constrained geometry catalyst system, designated herein as "CGC", as described above for Inventive Example 1. Comparative run 6 was manufactured in single-reactor slurry polymerization system using a 26 L CSTR (continuous stirred tank reactor) with adequate stirring to keep the particles in suspension. The reactor was jacketed to remove the heat of reaction and a constant flow of 5900 g/h of propane was fed to the reactor and a constant flow of nitrogen was fed into the vapor space of the reactor. The reactor over pressure was controlled by venting the gas and 2500 g/h of ethylene and 4.96 NL/h of hydrogen were injected below the liquid level using a common pipe. The CGC catalyst was injected, along with liquid propane diluent, below the liquid level. The CGC catalyst concentration in the catalyst vessel was 0.8 wt. % in hexane and solids were withdrawn intermittently. For the manufacture, the reactor temperature was held at 70° C. and pressure was held at 55 barg. The reactor was operated at an average residence time of 60 minutes and the resulting polymer production rate was 714 g/h while the catalyst efficiency was calculated to be 170,813 g PE/g Ti. Details of the process conditions used to manufacture comparative run 6 can be found in Table 14. Comparative run 6 was a high density product and had an I.sub.2 melt index of 119 g/10 minutes and a density of 0.9731 g/cm.sup.3.

DETD Comparative run 7 was produced using the same catalyst system and polymerization system as comparative run 6, except 163.4 g/h of hexene was fed to the reactor and hydrogen flow was very low and was diluted with nitrogen. The average residence time for the manufacture of comparative run 7 was 60 minutes and the polymer production rate was 441 g/h while catalyst efficiency was calculated to be 150,000 g PE/g Ti. Comparative run 7 was an ethylene/1-hexene copolymer and had an I.sub.21.6 melt index of 0.25 g/10 minutes and a density of 0.9235 g/cm.sup.3.

DETD
TABLE 17

	Example	
	comp. run 3	comp. run 4

comp. run 6 comp. run 7

Process conditions and gas analysis for Single Reactor Products
Catalyst NDA NDA
CGC CGC
Process P [barg] 12 12
55 55
Conditions T deg C. 88 70
70 70
C.sub.6 flow [g/h] 1501 2800
Propane flow [g/h]
5902 5902
Tau [min] 82 48
60 60
Gas N.sub.2 [V %] 0.87 0.8533
77.11 78.14
Analysis H.sub.2 [V %] 69.47 4.746
0.04 0.002
C.sub.2 [V %] 19.89 82.206
10.70 11.56
C.sub.2H.sub.6 [V %] 1.07 0.04052
C.sub.4 [V %] 0.01 5.152
Isopentane [V %] 0.01 0.7445
C.sub.6 [V %] 1.44 9.452
0.07 0.03
C.sub.3H.sub.6 [V %] 0.22 0.2034
C.sub.3H.sub.8 [V %] 0.01 0.009156
12.50 10.80
H.sub.2/C.sub.2 gas phase ratio [mol %/mol %] 3.511
0.057733012 0.003383 0.000173
C.sub.4/C.sub.2 gas phase [mol %/mol %] 0.000
0.062671824
Process conditions and Product Properties for
Single Reactor Products
Process C.sub.2 flow start [g/h] 68.66 230
2497.00 2497.00
Flows H.sub.2 flow [Nl/h] 140.42 7.213
4.96 0.00
C.sub.2 flow [g/h] 816.23 856.475
2497.00 2497.00
C.sub.4 flow (AK 3) [g/h] 0.00 199.941
hexene flow [g/h]
0.00 163.44
Catalyst flow [micromolTi/h] 62.06 21.2
87.36 61.30
Hexane flow [g/h] 207.90 71.02
5902 (C3), 896 (C6) 5902 (C3), 628.3 (C6)
Product Powder (before Melt Index, 94
100
Properties compounding) I.sub.2g/10 min
Melt Index, I.sub.21.6,
0.38 0.33
g/10 min
Density, g/cm.sup.3 0.9306
0.9285
DETD
TABLE 19

Product Performance Properties
Example

		Comp. run 8	Inventive Ex 9	Inventive Ex 10	Inventive Ex 11	Inventive Ex
Mixture	48%/52%	NDA/NDA	CGC/NDA	NDA/CGC	CGC/CGC	
Melt Index						
I.sub.5	g/10 min.	0.32	0.43		0.27-0.27	0.31
I.sub.21.6	g/10 min.	8.64	9.97		4.11-4.09	5.24
I.sub.21.6/I.sub.5	Ratio	27.00	23.19		15.22-15.15	16.90
Density	g/cm.sup.3	0.9519	0.9528	0.9506	0.9505	
RCD		No	No	Yes	Yes	
Bohlin Rheology						
viscosity @ .1/s	Pa.s	74251	60151	66489	61290	
viscosity @ 100/s	Pa.s	2298	2110	3006	3085	
Power law K		28047	23925	32067	30370	
Power law n		0.4817	0.5077	0.5304	0.5439	
Tensile properties						
Yield stress	MPa	25.4	25.1	24.7	24.6	
Young's modulus	MPa	1072	1011	946	960	
3 Point Flex. Young's modulus	MPa	986	910	837	848	
Izod Impact	kJ/m.sup.2	22.1	17.1	34.7	42.7	
Rapid Crack propagation Gc ductile --brittle						
20	kJ/m.sup.2	14.8	21.4	24.0	38.9	
0	kJ/m.sup.2	10.9				
-5	kJ/m.sup.2	9.6				
-10	kJ/m.sup.2	8.8		10.5	20.9	
-15	kJ/m.sup.2	7.5		8.5		
-20	kJ/m.sup.2	6.6	11.8	7.6	19.3	
-30	kJ/m.sup.2	6.4	10.0		17.3	
-40	kJ/m.sup.2		7.7		12.9	
-50	kJ/m.sup.2		7.3		10.4	
-60	kJ/m.sup.2			6.3	10.3	
T.sub.db	° C.	-12	-35	-17	-45	
Slow Crack Growth	Minutes	59700	16362	>110000		

>110000
PENT
GPC

M.sub.n 19700	11700	14100	7660
M.sub.w 218900	198800	271600	233100
M.sub.w/M.sub.n 11.11	16.99	19.26	30.43
M.sub.z 732600	797100	2183000	757000

DETD While the invention has been described with respect to a limited number of embodiments, the specific features of one embodiment should not be attributed to other embodiments of the invention. No single embodiment is representative of all aspects of the inventions. Moreover, variations and modifications therefrom exist. For example, the polyethylene composition may comprise a third component, either ethylene homopolymer or copolymer, which makes the composition tri-modal in the overall molecular weight distribution. Similarly, a fourth, fifth, or sixth component may also be added to adjust the physical properties of the composition. Various additives may also be used to further enhance one or more properties. In other embodiments, the composition consists essentially of the LMW component and the HMW component described herein. In some embodiments, the composition is substantially free of any additive not specifically enumerated herein. In certain embodiments, the composition is substantially free of a nucleating agent. Cross-linking by physical or chemical methods may be another way to modify the composition. The appended claims intend to cover all such variations and modifications as falling within the scope of the invention.

CLM What is claimed is:
1. A polyethylene composition comprising a low-molecular-weight (LMW) ethylene homopolymer component and a high-molecular-weight (HMW) ethylene interpolymer component, and wherein the LMW component has a molecular weight distribution, MWD.sup.L, of less than about 8, and wherein the HMW component has a molecular weight distribution, MWD.sup.H less than about 5 and has a substantially uniform comonomer distribution, or wherein the HMW component has a reverse comonomer distribution.

27. A polyethylene composition comprising a low-molecular-weight (LMW) ethylene homopolymer component, and a high-molecular-weight (HMW) ethylene interpolymer component, and wherein the LMW component has a molecular weight distribution, MWD.sup.L, of less than about 8, and wherein the same catalyst system is used to make the LMW component and the HMW component, and wherein the composition has a molecular weight distribution less than 17.5.

28. A polyethylene composition comprising a low-molecular-weight (LMW) ethylene homopolymer component, and a high-molecular-weight (HMW) ethylene interpolymer component, and wherein the LMW component is characterized as having a molecular weight distribution, MWD.sup.L, of less than about 8, and wherein the LMW component is prepared from a constrained geometry catalyst.

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L5 ANSWER 18 OF 21 USPAT2 on STN

ACCESSION NUMBER: 2004:335871 USPAT2
TITLE: Multimodal polyolefin pipe
INVENTOR(S): Schramm, Detlef, Sehoenenberg, SWITZERLAND
Quack, Wolfgang, Mettmann, GERMANY, FEDERAL REPUBLIC OF
Damen, Julien, Mettmenstetten, SWITZERLAND
Cham, Pak-Meng, Lake Jackson, TX, UNITED STATES
PATENT ASSIGNEE(S): Dow Global Technologies, Inc., Midland, MI, UNITED STATES (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 7250473	B2	20070731	
	WO 2003020821		20030313	
APPLICATION INFO.:	US 2002-484906		20020828	(10)
	WO 2002-US27503		20020828	
			20040810	PCT 371 date

	NUMBER	DATE
PRIORITY INFORMATION:	US 2001-316401P	20010831 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Rabago, Roberto
NUMBER OF CLAIMS: 9
EXEMPLARY CLAIM: 1
LINE COUNT: 708
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention relates to a polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it has a density in the range of from about 0.925 g/ccm to about 0.950 g/ccm, a melt index (I.sub.2) in the range of from about 0.05 g/10 min to about 5 g/10 min, and in that it comprises at least one high molecular weight (HMW) ethylene interpolymer and at least a low molecular weight (LMW) ethylene polymer, and a composition comprising such resin. Also provided is a shaped article comprising said resin or composition, in particular a pipe.

SUMM The present invention provides a polyethylene resin with a multimodal molecular weight distribution. Said multimodal polyethylene resin is characterized in that it has a density in the range of from about 0.925 g/ccm to about 0.950 g/ccm and a melt index in the range of from about 0.05 g/10 min to about 5 g/10 min.

SUMM Unless expressly specified otherwise, the term "melt index" means the I.sub.2 melt index, as determined in accordance with ASTM D1238 under a load of 2.16 kg and at a temperature of 190° C.

SUMM The present invention provides a polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it has

(a) a density in the range of from about 0.925 g/ccm, preferably of from about 0.935 g/ccm, to about 0.950 g/ccm, preferably to about 0.945 g/ccm, and
(b) a melt index (I.sub.2) in the range of from about 0.05 g/10 min, preferably of from about 0.1 g/10 min, to about 5 g/10 min, preferably to about 1 g/10 min.

SUMM Said multimodal polyethylene resin comprises at least one high molecular weight (HMW) ethylene interpolymer and at

least a low molecular weight (LMW) ethylene polymer. The HMW interpolymer has a significantly higher weight average molecular weight than the LMW polymer. Said difference in molecular weight is reflected in distinct melt indices. Preferred is a multimodal polyethylene resin which has a trimodal or, most preferably, a bimodal molecular weight distribution. A bimodal polyethylene resin according to the present invention consists of one unimodal HMW ethylene interpolymer and one unimodal LMW ethylene polymer.

SUMM The HMW component characterizing the multimodal polyethylene resin of the invention comprises at least one or more, preferably one HMW ethylene interpolymer. Such ethylene interpolymer is characterized by a density in the range of from about 0.910 g/ccm, preferably of from about 0.915 g/ccm, to about 0.935 g/ccm, preferably to about 0.925 g/ccm, and a melt index of about 1.0 g/10 min or lower, preferably of about 0.05 g/10 min or lower. Advantageously, the HMW ethylene interpolymer has a melt index of about 0.02 g/10 min or higher. The HMW ethylene interpolymer contains ethylene interpolymerized with at least one alpha-olefin, preferably an aliphatic C.sub.4-C.sub.20 alpha-olefin, and/or a non-conjugated C.sub.6-C.sub.18 diolefin, such as 1,4-hexadiene or 1,7-octadiene. Although the HMW interpolymer can be a terpolymer, the preferred interpolymer is a copolymer of ethylene and an aliphatic alpha-olefin, more preferably such an alpha-olefin which has from four to ten carbon atoms. Particularly preferred aliphatic alpha-olefins are selected from the group consisting of butene, pentene, hexene, heptene and octene. Advantageously, the HMW component is present in an amount of from about 30 weight percent, preferably of from about 40 percent, to about 60 weight percent, preferably to about 50 percent (based on the total amount of polymer in the multimodal polyethylene resin). More preferably, the HMW component is present in an amount of from about 40 to about 55 percent. The molecular weight distribution as reflected by the M.sub.w/M.sub.n ratio of the HMW component is relatively narrow, preferably less than about 3.5, more preferably less than about 2.4.

SUMM The LMW component characterizing the multimodal polyethylene resin of the invention comprises at least one or more, preferably one LMW ethylene polymer. The LMW ethylene polymer is characterized by a density in the range of from about 0.945 g/ccm to about 0.965 g/ccm and a melt index of at least about 2.0 g/10 min or higher, preferably of at least about 5 g/10 min, more preferably of at least about 15 g/10 min or higher. Advantageously, the LMW component has a melt index of less than 2000 g/10 min, preferably of less than 200 g/10 min. A preferred LMW ethylene polymer is an ethylene interpolymer having a density in the range of from about 0.950 g/ccm to about 0.960 g/ccm and a melt index of at least about 2 g/10 min, preferably in the range of from about 10 g/10 min to about 150 g/10 min. Preferred LMW ethylene interpolymers are ethylene /alpha-olefin copolymers, particularly such copolymers wherein the aliphatic alpha-olefin comonomer has from four to ten carbon atoms. The most preferred aliphatic alpha-olefin comonomers are selected from the group consisting of butene, pentene, hexene, heptene and octene. Advantageously, the LMW component is present in an amount of from about 40 weight percent, preferably of from about 50 percent, to about 70 weight percent, preferably to about 60 percent (based on the total

amount of polymers comprised in the multimodal polyethylene resin of the invention). More preferably, the LMW component is present in an amount of from about 45 to about 60 percent.

SUMM While the alpha-olefins incorporated into a HMW component and into a LMW component comprised in a multimodal polyethylene resin of the invention may be different, preferred are such multimodal polyethylene resins, wherein the HMW and the LMW interpolymers incorporate the same type of alpha-olefin, preferably 1-butene, 1-pentene, 1-hexene, 1-heptene or 1-octene. Typically, the comonomer incorporation in the HMW ethylene interpolymer is higher than in the LMW polymer.

SUMM Preferably, the HMW component and the LMW component are each unimodal. The MWD in the GPC curves of the individual components, e.g. the HMW component and the LMW component, respectively, does not substantially exhibit multiple component polymers (i.e. no humps, shoulders or tails exist or are substantially discernible in the GPC curve). Each molecular weight distribution is sufficiently narrow and their average molecular weights are different. The ethylene interpolymers suitable for use as HMW and/or LMW component include both homogeneously branched (homogeneous) interpolymers and heterogeneously branched (heterogeneous) interpolymers.

SUMM Homogeneous ethylene interpolymers for use in the present invention encompass ethylene-based interpolymers in which any comonomer is randomly distributed within a given interpolymer molecule and wherein all of the interpolymer molecules have substantially the same ethylene/comonomer ratio. Homogeneous ethylene interpolymers are generally characterized as having an essentially single melting (point) peak between -30° C. and 150° C., as determined by differential scanning calorimetry (DSC). Typically, homogeneous ethylene interpolymers also have a relatively narrow molecular weight distribution (MWD) as compared to corresponding heterogeneous ethylene interpolymers. Preferably, the molecular weight distribution defined as the ratio of weight average molecular weight to number average molecular weight (M.sub.w/M.sub.n), is less than about 3.5. Furthermore, the homogeneity of the ethylene interpolymers is reflected in a narrow composition distribution, which can be measured and expressed using known methods and parameters, such as SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Breadth Index). The SCBDI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (typically abbreviated as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), in U.S. Pat. No. 4,798,081 (Hazlitt et al.), or in U.S. Pat. No. 5,089,321 (Chum et al.), the disclosures of all of which are incorporated herein by reference. CDBI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The SCBDI or CDBI for the homogeneous ethylene/alpha-olefin interpolymers used in the present invention is typically higher than about 50 percent.

SUMM The homogeneous ethylene interpolymers which can be used in the present invention fall into two categories, the linear homogeneous ethylene interpolymers and the substantially linear homogeneous ethylene interpolymers. Both are known in the art and commercially

available.

SUMM Homogeneous linear ethylene interpolymers are interpolymers which have a homogeneous short chain branching distribution and lack measurable or detectable long chain branching. Such homogeneous linear ethylene interpolymers can be made using polymerization processes which provide a uniform branching distribution, e.g., the process described by Elston in U.S. Pat. No. 3,645,992, who uses soluble vanadium catalyst systems. Other single-site catalyst systems including metallocene catalyst systems, e.g., of the type disclosed in U.S. Pat. No. 4,937,299 to Ewen et al., or U.S. Pat. No. 5,218,071 to Tsutsui et al., are also suitable for the preparation of homogeneous linear ethylene interpolymers.

SUMM The substantially linear ethylene interpolymers (SLEPs) are homogeneous interpolymers having long chain branching, meaning that the bulk ethylene interpolymer is substituted, on average, with about 0.01 long chain branches/1000 total carbons to about 3 long chain branches/1000 total carbons (wherein "total carbons" includes both backbone and branch carbon atoms). Preferred polymers are substituted with about 0.01 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons, more preferably from about 0.05 long chain branches/1000 total carbons to about 1 long chain branched/1000 total carbons, and especially from about 0.3 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons. The presence of long chain branches in such ethylene interpolymers can be determined according to methods known in the art, such as gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV).

SUMM For substantially linear ethylene polymers, the presence of long chain branching is manifest from enhanced rheological properties which can be quantified and expressed, for example, in terms of gas extrusion rheometry (GER) results and/or melt flow ratio (I.sub.10/I.sub.2) increases. The melt flow ratio of the substantially linear ethylene/alpha-olefin interpolymers can be varied essentially independently of the molecular weight distribution (M.sub.w/M.sub.n ratio).

SUMM Substantially linear ethylene interpolymers are produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor (e.g., as disclosed in WO 93/07187, WO 93/07188, and WO 93/07189, the disclosure of each of which is incorporated herein by reference), but can also be produced using multiple reactors (e.g., using a multiple reactor configuration as described in U.S. Pat. No. 3,914,342, the disclosure of which is incorporated herein by reference) at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties. The multiple reactors can be operated in series or in parallel, with at least one constrained geometry catalyst employed in at least one of the reactors.

SUMM Heterogeneous ethylene-based polymers encompass ethylene /α-olefin interpolymers characterized as having a linear backbone and a DSC melting curve having a distinct melting point peak greater than 115° C. attributable to a high density fraction. Such heterogeneous interpolymers typically have a broader molecular weight distribution than comparable homogeneous interpolymers.

Typically, heterogeneous ethylene interpolymers have a CDBI of about 50% or less, indicating that such interpolymers are a mixture of molecules having differing comonomer contents and differing amounts of short chain branching. The heterogeneous ethylene polymers that can be used in the practice of this invention include those prepared with a coordination catalyst at high temperature and relatively low pressure. Ethylene polymers and copolymers prepared by the use of a (multi-site) coordination catalyst, such as a Ziegler-Natta catalyst or a Phillips catalyst, are generally known as linear polymers because of the substantial absence of branch chains of polymerized monomer units pendant from the backbone.

SUMM The HMW ethylene interpolymer can be a heterogeneous interpolymer or a homogeneous interpolymer, a homogeneous interpolymer being preferred. Particularly preferred HMW ethylene interpolymers are homogeneous, substantially linear HMW ethylene interpolymers. The LMW ethylene interpolymer can be a heterogeneous interpolymer or a homogeneous interpolymer, a heterogeneous interpolymer being preferred.

SUMM Monolayer pipes according to the present invention consist of one layer made from a composition according to the present invention comprising a multimodal polyethylene resin as provided herein and suitable additives typically used or suitable for pipe applications. Such additives include colorants and materials suitable to protect the bulk polymer from specific adverse environmental effects, e.g. oxidation during extrusion or degradation under service conditions, such as, for example, process stabilizers, antioxidants, pigments, metal de-activators, additives to improve chlorine resistance and UV protectors. Preferred multilayer composite pipes include metal plastic composite pipes and are pipes comprising one or more, e.g., one or two, layers comprising a composition according to the present invention and a barrier layer. Such pipes include, for example, three-layer composite pipes with the general structure PE/Adhesive/Barrier or Barrier/Adhesive/PE, or five-layer pipes with the general structure PE/Adhesive/Barrier/Adhesive/PE or Polyolefin/Adhesive/Barrier/Adhesive/PE. In these structures PE stands for polyethylene layers which can be made from the same or different polyethylene compositions, preferably a PE-RT comprising composition, including at least one multimodal polyethylene composition according to the present invention. Suitable polyolefins include, for example, high density polyethylene, polypropylene and polybutylene, homopolymers and interpolymers. Preferred is a multilayer composite pipe wherein at least the inner layer comprises a multimodal polyethylene resin according to the present invention in a non-crosslinked form. More preferred is a multilayer composite pipe, wherein both PE layers comprise a multimodal polyethylene resin according to the present invention. In multilayer pipes, e.g. in the three-layer and five-layer structures exemplified above, the barrier layer may be an organic polymer capable of providing the desired barrier properties, such as an ethylene-vinyl alcohol copolymer (EVOH), or a metal, for example, aluminum or stainless steel.

DETD Melt indices are expressed as I.sub.2 (determined according to ASTM D-1238, condition E, 190° C./2.16 kg). The ratio of I.sub.10 (measured according to ASTM D-1238, Condition N, 190° C./10 kg) to I.sub.2 is the melt flow ratio and designated as I.sub.10/I.sub.2.

DETD The multimodal polyethylene resin used in the experiments is a bimodal ethylene interpolymer having an I.sub.2 of 0.85 g/10 min, a density of 0.940 g/ccm and an I.sub.10/I.sub.2 of 9.8. The resin

is made by in-situ blending using (continuous) solution process technology and two sequentially operated reactors. The HMW ethylene interpolymer is a homogeneous, substantially linear ethylene/octene copolymer which is made in the primary reactor using a constrained geometry catalyst. Said HMW interpolymer has an I.sub.2 of 0.034 g/10 min and a density of 0.921 g/ccm. The weight average molecular weight is 228,000 and the Mw/Mn ratio is 2.1. The LMW ethylene polymer is a heterogeneous, linear ethylene/octene copolymer having an I.sub.2 melt index of 20 g/10 min and a density of 0.953 g/ccm. The weight average molecular weight of the LMW polymer is 52,100 and the Mw/Mn ratio is 3. The LMW ethylene polymer is made in the secondary reactor using a multi-site Ziegler-Natta (coordination) catalyst. The ratio of HMW copolymer to LMW copolymer in the bimodal polyethylene resin is 40 to 60.

CLM What is claimed is:

1. A polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it: (a) has a density in the range from 0.925 g/ccm to 0.950 g/ccm, and (b) has a melt index (I.sub.2) in the range from 0.1 g/10 min to 5 g/10 min, and (c) comprises a high molecular weight (HMW) component and a low molecular weight (LMW) component, and wherein the HMW component comprises at least one high molecular weight ethylene interpolymer having a density in the range from 0.910 g/ccm to 0.935 g/ccm, and a melt index of 1.0 g/10 min or lower, and wherein the LMW component comprises at least one low molecular weight ethylene polymer having a density in the range from 0.945 g/ccm to 0.965 g/ccm, and a melt index in the range from 2.0 g/10 min to less than 200 g/10 min, and wherein the at least one high molecular weight interpolymer and/or the at least one low molecular weight polymer is a homogeneous, substantially linear interpolymer.

8. The polyethylene resin according to claim 1, wherein the at least one low molecular weight ethylene polymer is an ethylene interpolymer that has a density of 0.960 g/ccm or lower.

9. The polyethylene resin according to claim 1, wherein the polyethylene resin has a bimodal molecular weight distribution, and wherein the resin consists of one unimodal high molecular weight ethylene interpolymer and one unimodal low molecular weight ethylene polymer.

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L5   ANSWER 15 OF 21  USPATFULL on STN
ACCESSION NUMBER:       97:94307  USPATFULL
TITLE:                  Process for producing an in situ polyethylene blend
INVENTOR(S):            Rifi, Mahmoud R., Kendall Park, NJ, United States
                        Martino, Carlo F., Somerville, NJ, United States
PATENT ASSIGNEE(S):     Union Carbide Chemicals & Plastics Technology
                        Corporation, Danbury, CT, United States (U.S.
                        corporation)

                             NUMBER        KIND     DATE
                        ---------------- ------ --------
PATENT INFORMATION:     US 5677375               19971014
APPLICATION INFO.:      US 1996-625612           19960329  (8)
```

S/N 10/568,739

	NUMBER	DATE
PRIORITY INFORMATION:	US 1995-1366P	19950721 (60)
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	Granted	
PRIMARY EXAMINER:	Delmendo, Romulo H.	
LEGAL REPRESENTATIVE:	Bresch, Saul R.	
NUMBER OF CLAIMS:	10	
EXEMPLARY CLAIM:	1	
LINE COUNT:	951	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB (a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series;

SUMM LLDPE resins designed for commodity type applications typically incorporate 1-butene as the comonomer. The use of a higher molecular weight alpha-olefin comonomer produces resins with significant strength advantages relative to those of ethylene/1-butene copolymers. The predominant higher alpha-olefin comonomer in commercial use are 1-hexene, 4-methyl-1-pentene, and 1-octene. The bulk of the LLDPE is used in film products where the excellent physical properties and drawdown characteristics of LLDPE film makes this film well suited for a broad spectrum of applications. Fabrication of LLDPE film is generally effected by the blown film and slot casting processes. The resulting film is characterized by excellent tensile strength, high ultimate elongation, good impact strength, and excellent puncture resistance.

SUMM The blending of these polymers is successfully achieved in a staged reactor process similar to those described in U.S. Pat. Nos. 5,047,468 and 5,149,738. Briefly, the process is one for the in situ blending of polymers wherein a higher density ethylene copolymer is prepared in a high melt index reactor and a lower density ethylene copolymer is prepared in a low melt index reactor. The process typically comprises continuously contacting, under polymerization conditions, a mixture of ethylene and one or more alpha-olefins with a catalyst system in two gas phase, fluidized bed reactors connected in series, said catalyst system comprising: (i) a supported magnesium/titanium based catalyst precursor; (ii) an aluminum containing activator compound; and (iii) a hydrocarbyl aluminum cocatalyst.

SUMM (a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series;

DETD The copolymers produced in each of the reactors are copolymers of ethylene and at least one alpha-olefin comonomer having 3 to 8 carbon atoms, preferably one or two alpha-olefin comonomers. The alpha-olefins can be, for example, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene.

DETD It will be understood that the in situ blend, which includes the aforementioned hydrocarbon(s) can be characterized as a trimodal resin. The properties of trimodal resins are strongly dependent on the proportion of the high molecular weight component, i.e., the low melt index component. For a staged reactor system, the proportion of the high molecular weight component is controlled via the relative production rate in each reactor. The relative production rate in each reactor can, in turn, be controlled by a computer application

program, which monitors the production rate in the reactors (measured by heat balance).

DETD A relatively low melt index (or relatively high molecular weight) copolymer is prepared in the first reactor. The first reactor is generally smaller in size than the second reactor because only a portion of the final product is made in the first reactor. The mixture of polymer and an active catalyst is usually transferred from the first reactor to the second reactor via an interconnecting device using nitrogen or second reactor recycle gas as a transfer medium. Alternatively, the low molecular weight copolymer is prepared in the first reactor and the high molecular weight copolymer is prepared in the second reactor.

DETD Because of the low values, instead of melt index, flow index is determined and those values are used in this specification. The flow index can be in the range of about 0.01 to about 30 grams per 10 minutes, and is preferably in the range of about 0.2 to about 12 grams per 10 minutes. The molecular weight of this polymer is, generally, in the range of about 135,000 to about 445,000. The density of the copolymer can be at least 0.860 gram per cubic centimeter, and is preferably in the range of 0.900 to 0.940 gram per cubic centimeter. The melt flow ratio of the polymer can be in the range of about 20 to about 70, and is preferably about 22 to about 45.

DETD Melt index is determined under ASTM D-1238, Condition E. It is measured at 190° C. and 2.16 kilograms and reported as grams per 10 minutes. Flow index is determined under ASTM D-1238, Condition F. It is measured at 190° C. and 10 times the weight used in determining the melt index, and reported as grams per 10 minutes. Melt flow ratio is the ratio of flow index to melt index.

DETD A relatively high melt index (or relatively low molecular weight) copolymer is prepared in this reactor. The high melt index can be in the range of about 50 to about 3000 grams per 10 minutes, and is preferably in the range of about 50 to about 1000 grams per 10 minutes. The molecular weight of the high melt index copolymer is, generally, in the range of about 15,800 to about 35,000. The density of the copolymer prepared in this reactor can be at least 0.900 gram per cubic centimeter, and is preferably in the range of 0.910 to 0.975 gram per cubic centimeter. The melt flow ratio of this copolymer can be in the range of about 20 to about 70, and is preferably about 20 to about 45.

DETD The blend or final product, as removed from the second reactor, can have a melt index in the range of about 0.02 to about 3.5 grams per 10 minutes, and preferably has a melt index in the range of about 0.04 to about 2.0 grams per 10 minutes. The melt flow ratio is in the range of about 55 to about 135, and is preferably in the range of about 55 to about 125. The molecular weight of the final product is, generally, in the range of about 90,000 to about 450,000. The density of the blend is at least 0.915 gram per cubic centimeter, and is preferably in the range of 0.916 to 0.960 gram per cubic centimeter.

DETD In the low melt index, as reflected in flow index, reactor, i.e., the first reactor:

DETD In the high melt index reactor, i.e., the second reactor:

DETD A technique for increasing the modality of the polyethylene and improving other properties thereof is to introduce various additives into the polyethylene. The preferred additive is a saturated alicyclic hydrocarbon. On addition of the hydrocarbon, the polyethylene or mixture of polyethylenes increase their modality, for example, from monomodal to bimodal and from bimodal

to trimodal. Thus, the post-blend polyethylene(s) can be characterized as multimodal.

DETD An in situ blend of two copolymers of ethylene and 1-hexene is prepared in two fluidized bed reactors with the following catalyst:

DETD The compounded resin is extruded into films on an Alpine.TM. extrusion line having a die size of 100 millimeters; a die gap of 1 millimeter; a screw size of 50 millimeters; and a frost line height (FLH) of about 7 to 10 times the die size, i.e., about 90 centimeters. The blow-up ratio is 4:1. The melt temperature is about 400 degrees F. The extrusion rate is 8 pounds per hour-inch of die circumference. The films are 1, 0.4, and 0.5 mil in thickness.

CLM What is claimed is:

1. A gas phase process for the production of an in situ polyethylene blend comprising contacting ethylene and at least one alpha-olefin comonomer having 3 to 8 carbon atoms with a magnesium/titanium based catalyst system including an activator and a cocatalyst in each of two fluidized bed reactors connected in series, under polymerization conditions, with the provisos that: (a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series; (b) other than the active catalyst referred to in proviso (a) and the cocatalyst referred to in proviso (f), no additional catalyst is introduced into the second reactor; (c) in the first reactor in which a relatively high molecular weight copolymer is made: (1) the alpha-olefin is present in a ratio of about 0.01 to about 0.4 mole of alpha-olefin per mole of ethylene; and (2) optionally, hydrogen is present in a ratio of about 0.0001 to about 0.3 mole of hydrogen per mole of ethylene; (d) in the second reactor in which a relatively low molecular weight copolymer is made: (1) the alpha-olefin is present in a ratio of about 0.005 to about 0.6 mole of alpha-olefin per mole of ethylene; and (2) hydrogen is present in a ratio of about 1 to about 3 moles of hydrogen per mole of ethylene; (e) a sufficient amount of one or more hydrocarbons is added to the first reactor or to the mixture formed in the first reactor prior to its introduction into the second reactor to provide about 0.5 to about 15 parts by weight of hydrocarbon(s) per 100 parts by weight of the in situ blend, each of said hydrocarbons being a saturated alicyclic hydrocarbon, which is liquid at the temperature at which polymerization is effected in the reactors, is essentially amorphous, and contains less than about 15 percent by weight paraffin wax; and (f) additional hydrocarbyl aluminum cocatalyst is introduced into the second reactor in an amount sufficient to restore the level of activity of the catalyst transferred from the first reactor to about the initial level of activity in the first reactor.

3. The process defined in claim 2 wherein the amount of hydrocarbon(s) introduced is about 3 to about 30 parts by weight of hydrocarbon(s) per 100 parts by weight of the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor.

4. The process defined in claim 2 wherein the polymer formed in the first reactor has a flow index in the range of about 0.01 to about 30 grams per 10 minutes and a density in the range of about 0.860 to about 0.940 gram per cubic centimeter and the polymer formed in the second reactor has a melt index in the range of about 50 to about 3000 grams per 10 minutes and a density in the range of about 0.900 to about 0.975 gram per cubic centimeter, the weight ratio of first reactor polymer to second reactor polymer being in the range of about 0.67:1 to about 2:1.

5. The process defined in claim 3 wherein the blend has a melt index in the range of about 0.02 to about 3.5 grams per 10 minutes; a melt flow ratio in the range of about 55 to about 135; and a density in the range of 0.915 to 0.960 gram per cubic centimeter.

7. The process defined in claim 6 wherein the blend has a melt index in the range of about 0.04 to about 2.0 grams per 10 minutes; a melt flow ratio in the range of about 55 to about 125; and a density in the range of 0.916 to 0.960 gram per cubic centimeter.

8. A gas phase process for the production of an in situ polyethylene blend wherein the polymer formed in the first reactor is a copolymer of ethylene, 1-hexene, and, optionally, one or more other up to 8 carbon atom alpha-olefins having a flow index in the range of about 0.2 to about 12 grams per 10 minutes and a density in the range of about 0.900 to about 0.940 gram per cubic centimeter and the polymer formed in the second reactor is a copolymer of ethylene, 1-butene and/or 1-hexene, and, optionally, one or more other up to 8 carbon atom alpha-olefins having a melt index in the range of about 50 to about 1000 grams per 10 minutes and a density in the range of about 0.910 to about 0.975 gram per cubic centimeter, the weight ratio of first reactor polymer to second reactor polymer being in the range of about 0.75:1 to about 1.6:1, comprising contacting ethylene and the aforementioned alpha-olefins with a magnesium/titanium based catalyst system including an activator and a cocatalyst in each of two fluidized bed reactors connected in series, under polymerization conditions, with the provisos that: (a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series; (b) other than the active catalyst referred to in proviso (a) and the cocatalyst referred to in proviso (f), no additional catalyst is introduced into the second reactor; (c) in the first reactor in which a relatively high molecular weight copolymer is made: (1) the alpha-olefin is present in a ratio of about 0.02 to about 0.26 mole of alpha-olefin per mole of ethylene; and (2) hydrogen is present in a ratio of about 0.017 to about 0.18 mole of hydrogen per mole of ethylene; (d) in the second reactor in which a relatively low molecular weight copolymer is made: (1) the alpha-olefin is present in a ratio of about 0.01 to about 0.42 mole of alpha-olefin per mole of ethylene; and (2) hydrogen is present in a ratio of about 1.7 to about 2.2 moles of hydrogen per mole of ethylene; (e) a sufficient amount of one or more hydrocarbons is added to the first reactor or to the mixture formed in the first reactor prior to its introduction into the second reactor to provide about 3 to about 12 parts by weight of hydrocarbon(s) per 100 parts by weight of the in situ blend, each of said hydrocarbons being a saturated alicyclic hydrocarbon, which is liquid at the temperature at which polymerization is effected in the reactors, is essentially amorphous, and contains less than about 15 percent by weight paraffin wax, said amount of hydrocarbon(s) added being in the range of about 3 to about 30 parts by weight of hydrocarbon(s) per 100 parts by weight of the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor; and (f) additional hydrocarbyl aluminum cocatalyst is introduced into the second reactor in an amount sufficient to restore the level of activity of the catalyst transferred from the first reactor to about the initial level of activity in the first reactor.

10. The process defined in claim 9 wherein the amount of hydrocarbon(s) introduced into the first reactor or prior to the second reactor is about 4 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor.

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L5   ANSWER 14 OF 21  USPATFULL on STN
ACCESSION NUMBER:       97:112415  USPATFULL
TITLE:                  High activity polyethylene catalysts which
                        produce bimodal or trimodal product molecular
                        weight distributions
INVENTOR(S):            Hagerty, Robert O., Metuchen, NJ, United States
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PATENT ASSIGNEE(S):     Mobil Oil Corporation, Fairfax, VA, United States (U.S.
                        corporation)

                             NUMBER        KIND    DATE
                        --------------- ------ --------
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APPLICATION INFO.:      US 1997-799086          19970211  (8)
RELATED APPLN. INFO.:   Continuation of Ser. No. US 1994-335624, filed on 8 Nov
                        1994, now abandoned which is a continuation-in-part of
                        Ser. No. US 1993-121821, filed on 15 Sep 1993, now
                        abandoned which is a continuation-in-part of Ser. No.
                        US 1993-8854, filed on 25 Jan 1993, now abandoned which
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NUMBER OF CLAIMS:       28
EXEMPLARY CLAIM:        1
NUMBER OF DRAWINGS:     8 Drawing Figure(s); 4 Drawing Page(s)
LINE COUNT:             849
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
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TI High activity polyethylene catalysts which produce bimodal or trimodal product molecular weight distributions

SUMM The present invention relates to a method for copolymerizing ethylene and alpha-olefins, a catalyst for such a copolymerization and a method for producing such a catalyst. A particular aspect of the present invention relates to a method for producing linear copolymers of ethylene and alpha-olefins of low density (LLDPE) with a density of less than about 0.93 g/cc, and medium density, (MDPE) with a density of 0.93 to 0.94 g/cc.

SUMM One of the measures of MWD of a LLDPE or MDPE resin is the melt

flow ratio (MFR), which is the ratio of the high-load melt index (HLMI or I.sub.21) to the melt index (MI or I.sub.2) for a given resin: MFR=I.sub.21 /I.sub.2. The MFR value is an approximate indication of MWD of a polymer: the higher the MFR value, the broader the MWD. All commercial polyethylene resins processed with high-stalk extrusion equipment have a relatively broad MWD as indicated by MFR values of 80-200. Although resins with relatively broad MWD exhibit good processability on high-stalk extrusion equipment, their film toughness properties, such as tear strength, are relatively poor.

DETD The molecular weight of the polymers may be controlled in a known manner, e.g., by using hydrogen. With the catalysts produced according to the present invention, molecular weight may be suitably controlled with hydrogen when the polymerization is carried out at relatively low temperatures, e.g., from about 70° to about 105° C. The molecular weight control is evidenced by an increase in the melt index of the polymer when the molar ratio of hydrogen to ethylene in the reactor is increased.

DETD The ethylene copolymers prepared in accordance with the present invention may be copolymers of ethylene with one or more C.sub.3 -C.sub.10 alpha-olefins. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/propylene copolymers, ethylene /1-butene copolymers, ethylene/1-hexene copolymers, ethylene/4-methyl-1-pentene copolymers, ethylene/1-butene/1-hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers. The most preferred polymers are copolymers of ethylene with 1-hexene, 1-butene or 4-methyl-1-pentene.

DETD The ethylene copolymers produced in accordance with the present invention preferably contain at least about 80 weight percent of ethylene units, and most preferably contain from 90 to 95 weight percent of ethylene units.

DETD ______________________________________

Density   ASTM D-1505 - A plaque is made and conditioned
          for one hour at 100° C. to approach equilibrium
          crystallinity. Measurement for density is
          then made in a density gradient column;
          reported as g/cc.
  Melt Index
          ASTM D-1238 - Condition E - Measured at
(MI), I.sub.2
          190° C. - reported as grams per 10 minutes.
High Load Melt
          ASTM D-1238 - Condition F - Measured at
(HLMI), Index
          10 times the weight used in the melt index
I.sub.21 test above.
  Melt Flow Ratio (MFR) = I.sub.21 /I.sub.2
Comonomer Comonomer contents of ethylene copolymers were
Content   measured by the infrared spectroscopic method,
          as described in the article of T. E. Nowlin,
          Y. V. Kissin and K. P. Wagner HIGH ACTIVITY
          ZIEGLER-NATTA CATALYST FOR THE
          PREPARATION OF ETHYLENE COPOLYMERS,
          Journal of Polymer Science: Part A:
          Polymer Chemistry, Volume 26, pages 755-764
          (1988).

Dart Impact
ASTM D1709 Free Falling DART Method (F50)
Tear Strength
ASTM D-1922

DETD Six different catalyst precursors of Examples 1-6 were evaluated with DMAC as cocatalyst in order to determine the effect of the catalyst type on the fraction of high molecular weight (HMW) component in the polymer. The laboratory slurry polymerization data is summarized in Table I. Typical slurry polymerization conditions in these experiments, as described for Catalyst precursor D were as follows: A 1.6-liter stainless steel autoclave, at 53° C., was filled with 0.750 liter of dry heptane, 0.120 liter of dry 1-hexene, and 3.0 mmol of DMAC was added while under a slow nitrogen purge. The stirring rate was set at about 900 rpm, the internal temperature was increased to ca. 85° C., and the internal pressure was raised from 8 psi to 59 psi with hydrogen. Ethylene was introduced to maintain the total pressure at 200 psi. Next, 0.0192 g of Catalyst precursor D was introduced into the reactor with ethylene over-pressure and the temperature was maintained at 85° C. for 60 minutes, then the ethylene supply was stopped and the reactor was allowed to cool to room temperature. A yield of 59.4 g of polyethylene was collected. The high-load flow index (HLMI) of this polymer was 8.67, the Melt Flow Ratio was 38.0, and the polymer contained 1.4 mol % of 1-hexene. The GPC chromatograms of the polymers prepared with each type of catalyst are illustrated in FIGS. 1-6.

DETD Ethylene/1-hexene copolymers were prepared with these catalysts under the same polymerization conditions. A typical example is shown below.

DETD Given below are the catalyst productivities and polymer flow indexes and melt flow ratios (I.sub.21 /I.sub.2). The catalysts were prepared according to the sequence.

CLM What is claimed is:
1. A catalyst composition for producing, in a single reactor, a product with bimodal or trimodal molecular weight distribution, selected from the group consisting of polymers and copolymers of ethylene, wherein the product is characterized by a density in a range of from 0.918 to 0.949 g/cc and by MFR value in a range of from 28 to 70, said MFR value being a ratio of I.sub.21 /I.sub.2, wherein I.sub.2 and I.sub.21 are melt indices which are measured according to ASTM D-1238, Conditions E and F; wherein said product contains from 5 to 50 weight percent of a component with a molecular weight higher than 700,000; wherein the catalyst composition is formed by steps comprising: (i) providing a slurry, in a non-polar solvent, of porous silica having hydroxyl groups on its surface; (ii) impregnating said silica with an organomagnesium compound RMgR' to form an intermediate (ii), wherein R and R' are alkyl groups of 4 to 10 carbon atoms and are the same or different; wherein said RMgR' is soluble in said non-polar solvent; and wherein the molar ratio of the hydroxyl groups to magnesium is less than 1; (iii) treating intermediate (ii) with carbon tetrachloride to form an intermediate (iii); wherein the amount of carbon tetrachloride is effective to provide a CCl.sub.4 to organomagnesium compound molar ratio of 0.3 to 3.0; (iv) treating intermediate (iii) with titanium tetrachloride and removing said non-polar solvent from the slurry to form a solid catalyst precursor; wherein the amount of titanium tetrachloride is effective to provide a Ti:hydroxyl group molar ratio of greater than 1.0; and (v) combining said solid catalyst precursor with dimethylaluminum chloride as cocatalyst; wherein the amount of cocatalyst is effective to provide

an Al:Ti molar ratio of greater than 10.

15. A catalyst composition for producing, in a single reactor, a product with bimodal or trimodal molecular weight distribution, selected from the group consisting of polymers and copolymers of ethylene, wherein the product is characterized by a density in a range of from 0.918 to 0.949 g/cc and by MFR value in a range of from 28 to 70, said MFR value being a ratio of I.sub.21 /I.sub.2, wherein I.sub.2 and I.sub.21 are melt indices which are measured according to ASTM D-1238, Conditions E and F; wherein said product contains from 5 to 50 weight percent of a component with a molecular weight higher than 700,000; wherein the catalyst composition is formed by steps comprising: (i) providing a slurry, in a non-polar solvent, of porous silica having hydroxyl groups on its surface; (ii) impregnating said silica with an organomagnesium compound RMgR' to form an intermediate (ii), wherein R and R' are alkyl groups of 4 to 10 carbon atoms and are the same or different; wherein said RMgR' is soluble in said non-polar solvent; and wherein the molar ratio of the hydroxyl groups to magnesium is less than 1; (iii) treating intermediate (ii) with 1,1,1-tetrachloroethane to form an intermediate (iii); wherein the amount of 1,1,1-tetrachloroethane is effective to provide a CCl.sub.3 CH.sub.3 to organomagnesium compound molar ratio of 0.3 to 3.0; (iv) treating intermediate (iii) with titanium tetrachloride and removing said non-polar solvent from the slurry to form a solid catalyst precursor; wherein the amount of titanium tetrachloride is effective to provide a Ti:hydroxyl group molar ratio of greater than 1.0 to form said solid catalyst precursor; and (v) combining said solid catalyst precursor with dimethylaluminum chloride as cocatalyst; wherein the amount of cocatalyst is effective to provide an Al:Ti molar ratio of greater than 10.

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COST IN U.S. DOLLARS                              SINCE FILE     TOTAL
                                                       ENTRY   SESSION
FULL ESTIMATED COST                                   150.77    151.19

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                                                       ENTRY   SESSION
FULL ESTIMATED COST                                     0.42    151.61

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